AN IMPROVED NMR SCAL TECHNIQUE

Hege Christin Widerøe[1], Geir Humborstad Sørland[2], Henrik Walbye Anthonsen[3], and Åsmund Ukkelberg[4]

[1] Statoil ASA, [2] Anvendt Teknologi AS, [3] Anthonsen Analyse&Data, [4] Dep. Of Chemistry University of Oslo, Norway

This paper was prepared for presentation at the International Symposium of the Society of Core Analysts held in Trondheim, Norway 12-16 September, 2006

ABSTRACT

On a set of rock core plugs saturated with brine, we have applied various two dimensional NMR techniques in order to extract more information than from ordinary one dimensional NMR techniques. One of the NMR techniques has been optimised for probing the coating of minerals on the surfaces within the rock core plugs.

INTRODUCTION

One of the major challenges in applying NMR measuring techniques is to choose the right applications for a given task. The result from an NMR experiment is particularly sensitive to the viscosity of the components within the rock, the electromagnetic properties of the rock and the dimension and type of cavities within the porous rock. When performing NMR diffusion experiments we are able to probe the viscosity of the fluid components, when performing a NMR experiment with variable inter echo spacing we are able to probe the electromagnetic properties, and when combining NMR diffusion and relaxation time experiments we are able to produce a pore size distribution for the rock. In the following we will focus on an application that is optimised for indicating the degree of surface coating within a rock core plug.

SURFACE COATING INDICATOR

The typical T_2 measurement from a water saturated core plug results in a distribution containing a main peak with a significant left shoulder. Occasionally this shoulder appears as a peak, which may indicate a separate region at shorter T_2 values. The ordinary T_2 experiment usually correlates to the product of surface relaxivity and the pore size distribution (Brownstein et al (1979))

$$\frac{1}{T_2} = \frac{1}{T_2^{bulk}} + \rho\frac{S}{V} \qquad [1]$$

where ρ is the surface relaxation strength and S/V is the surface to volume ratio (which correlates to the pore sizes). An internal magnetic field gradient is generated by the magnetic susceptibility differences throughout the sample when it is placed in an external homogeneous magnetic field (Drain (1962))

$$G_i \approx \frac{B_0 \Delta\chi}{R} \qquad [2]$$

where ***R*** is the distance over which the magnetic field varies, B_0 is the applied magnetic field, and $\Delta\chi$ is the difference in susceptibility between the surface of the solid matrix and the water. Thus the presence of internal magnetic field gradients requires another relaxation term to be added to Equation1; dephasing of the nuclear magnetisation due to diffusion in the presence of an internal magnetic field gradient $\mathbf{G_i}$:

$$\frac{1}{T_2} = \frac{1}{T_2^{bulk}} + \rho\frac{S}{V} + \frac{\tau^2(\gamma G_i)^2 D}{3} \qquad [3]$$

where γ is the gyromagnetic ratio, D is the diffusion coefficient, and τ is the inter echo spacing illustrated in Figure 1. In principle the internal magnetic field gradient may be measured by varying the inter echo spacing for the first spin echo in the CPMG train (Figure 1), while keeping the other inter echo spacing at a constant value. Application of a 2 Dimensional Inverse Laplace Transform (2D-ILT) on the data sets would then result in the following values for the T_2 and ψ axis (assuming $T_2^{bulk} >> T_2$)

$$T_2 = \frac{r_{pore}}{\rho} \quad \text{and} \quad \psi = \frac{3}{(\gamma G_i)^2 D} \qquad [4]$$

Assuming that the diffusion coefficient is close to the bulk value throughout the sample, $\mathbf{G_i}$ can be found and will correlate to the inverse of the typical distance defined in Equation 2. As the pore radii characterise the typical distance over which the magnetic field varies ($\mathbf{R \approx r_{pore}}$), a distribution of $\mathbf{G_i}$ yields direct information of the porous structure. The product $\mathbf{G_i * r_{pore}}$ is thus mainly dependent on the magnetic susceptibility changes between the solid matrix and the water (see Equation 2)

$$G_i * R \approx G_i * r_{pore} \approx B_0 * \Delta\chi$$
$$\Downarrow$$
$$G_i * \frac{r_{pore}}{\rho} \approx B_0 * \left(\frac{\Delta\chi}{\rho}\right)$$
$$\Downarrow$$
$$G_i * T_2 \approx B_0 * \left(\frac{\Delta\chi}{\rho}\right) = K_{gi} \qquad [5]$$

Where Equation 5 defines the surface coating indicator K_{gi} .

From Equation 5 one may conclude that for a given pore structure, a variation in the product between $\mathbf{G_i}$ and T_2 must be caused by a difference in properties at the surface of

the porous rock and/or the interface between the solid and the liquid in the pores within the solid matrix. In the following we will consider $\mathbf{G_i}$ to be given by Equation 2. This is truly an approximation as there evidently will be a variation of $\mathbf{G_i}$ dependent on the complexity of the porous structure and on the distribution of solid compounds (as for example chlorite) within the porous rock, Zhang and Hirasaki (2003), Zielinski and Sen (2003). In addition there will be an averaging effect on $\mathbf{G_i}$ due to diffusion during the time between the spin echoes in the CPMG sequence (Figure 1). However, as will be shown in the results section, we are able to extract new and vital information on the rock core samples from the approximations leading to Equation 5.

EXPERIMENTAL: THE SE-CPMG METHOD

Figure 1 displays a NMR pulse sequence that will extract information regarding the porous structure and paramagnetic impurities on the surface of the solid matrix. The optimisation of this experiment is based on varying the first inter echo spacing in the sequence (τ'), and to fit all experiments as a function of observation time to get the initial NMR signal undistorted by relaxation at the shortest spacing (τ). All information obtainable is thus preserved, which is especially important in systems exhibiting T_2 distribution shifted towards short T_2 values. The attenuation is written

$$I = I_0 \exp^{-(2\tau')\left(\frac{1}{T_2^{bulk}} + \rho\frac{S}{V} + \frac{\tau'^2(\gamma G_i)^2 D}{3}\right)} \exp^{-(2n\tau)\left(\frac{1}{T_2^{bulk}} + \rho\frac{S}{V} + \frac{\tau^2(\gamma G_i)^2 D}{3}\right)} \quad [6]$$

The experiment will return a data matrix where the attenuation is due to T_2 along the columns (as a function of observation time (2nτ)), while the attenuation is due to surface relaxivity and internal magnetic field gradients along the rows. When assuming the surface relaxivity to be not significantly dependent on the inter echo spacing, the attenuation along the rows will be a function of τ'^3.

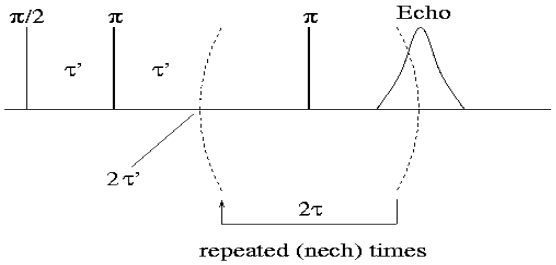

Figure 1: The Single Spin Echo CPMG (SE-CPMG) experiment

The NMR instrument is a Maran DRX 1.5 inch bench top from Resonance Instruments operating at a proton frequency of 2 MHz. The samples studied were 1.5" sandstone plugs. In the bulk mineralogy of the sandstones quartz represents the major component (up to 73 % in weight). Also found by XRD were significant amounts of feldspar, mica, illite and chlorite/kaolinite.

RESULTS FROM BRINE SATURATED ROCK CORE PLUGS

In Table 1 the major results from a set of brine saturated sandstone plugs are displayed. Due to position of the peaks along the G_i axis (Figure 2), we have defined 4 subclasses of cavities; clay, small, medium and large. As seen from one of the plugs in Figure 2, four regions within the $(1/G_i)^2$ distribution are present while we see only two distinct regions within the T_2 distribution.

Table 1: Mean values of internal magnetic field gradients (Gauss/cm) and T_2 (ms), NR = Not Resolved, NP = Not Present), Helium porosity (%) and permeability (mD)

ID	G_i Clay	G_i Small	G_i Med.	G_i Large	T_2 Clay	T_2 Small	T_2 Med.	T_2 Large	Kg_i Average	Helium porosity / %	Air perm. / mD
1	NP	473.4	63.5	0.90	NP	1.5	11.1	233.5	0.328	13	0.21
2	1913	690	101.7	1.10	1.1	2.8	29.2	223.0	1.308	19	39
3	1033 (NR)	1033 (NR)	155.6	1.12	2.1 (NR)	2.1 (NR)	22.2	267.9	1.104	21	445
4	2310	600	77.8	1.03	0.4	1.2	5.3	230.3	0.526	10	0.66
5	1934	153.4 (NR)	153.4 (NR)	1.08	0.7	6.2 (NR)	6.2 (NR)	245.0	0.481	17	44
6	547.4 (NR)	547.4 (NR)	75.6	1.43	4.3 (NR)	4.3 (NR)	52.2	199.2	1.958	23	676
7	2160	381	50.7	1.18	2.5	12.2	63.9	283.7	3.066	17	190

A striking effect from the definition of K_{gi} is that the plug where the strongest internal magnetic field gradient is measured does not have a high value of K_{gi}. Thus it is not expected to have the largest difference in magnetic susceptibility between the surface of the solid matrix and the brine, and one may conclude that a measure of G_i only is not a good surface coating indicator. Basically what we do when measuring K_{gi} is to scale the measured internal magnetic field gradient against the expected pore size. Then we rule out the effect of different pore sizes on K_{gi}, and make it mainly sensitive to a varying magnetic susceptibility at the interface between the pore cavity and the solid matrix of the porous rock. When combining a single spin echo having variable inter-echo spacing with a train of spin echoes with fixed inter-echo spacing, we are therefore able to distinguish between brine saturated rock core plugs having different mineral surface coating. The reason why the experiment displayed in Figure 1 returns more information than an ordinary CPMG experiment is found in the attenuation of the spin echo NMR signal as a function of the square of the internal magnetic field gradient and the τ'^3 dependency. As there is a correlation between the internal magnetic field gradient and the pore structure, the square of this dependency will resolve different porous structures better than the CPMG, where there is a linear dependency between T_2 and the porous structure (Equation 1).

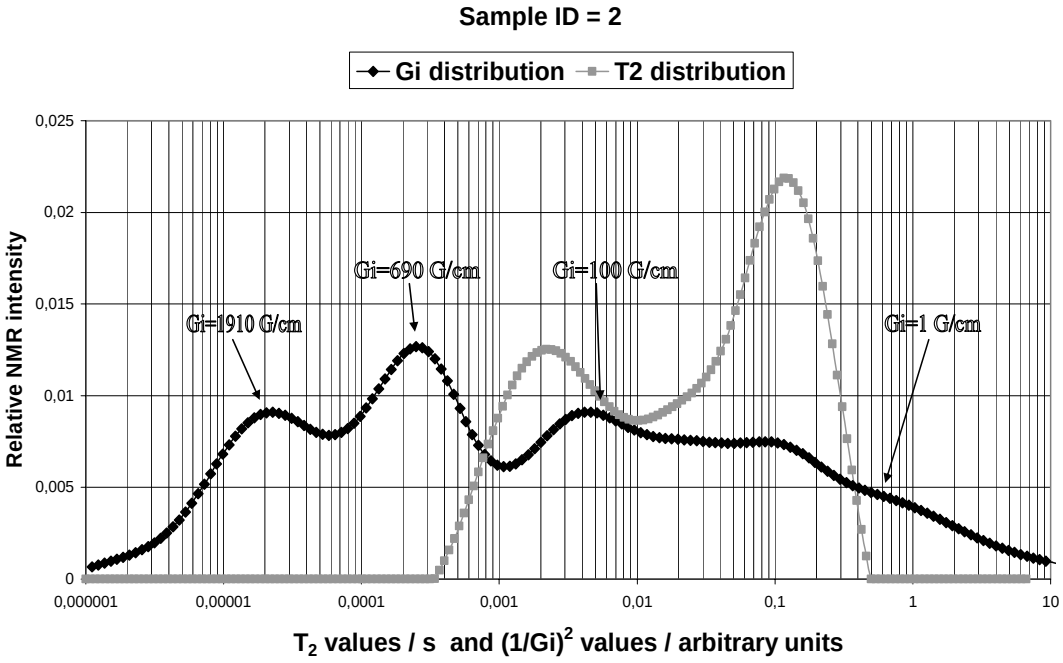

Figure 2: T_2 distribution (in seconds) and its corresponding $(1/G_i)^2$ distribution of a brine saturated rock core plug

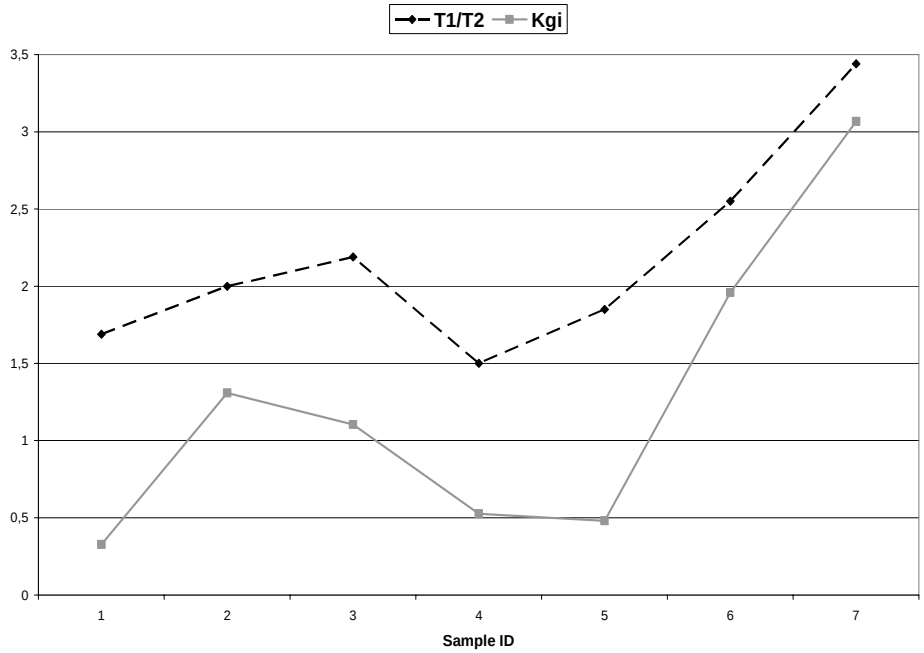

Figure 3: The mean values of (T_1/T_2) and K_{gi}. A linear correlation yields $R^2 = 0.94$.

Due to a τ'^3 dependency on the time parameter in the spin echo attenuation, it is possible to span most of the distribution in the internal gradients, even though the time domain in the CPMG varies from 0.2 ms up to seconds. When τ varies from 0.2 to 10 ms, it gives a variation in τ'^3 from 0.008 to 1000, which spans broader than the ordinary CPMG.

Correlations Between (T_1/T_2) And K_{gi}

It has been shown previously by Rueslåtten et al (1998) that the average T_1/T_2 correlates to the chlorite content. To verify that the Kgi actually does work as a surface coating indicator, the T_1/T_2 ratio was measured using a two dimensional experiment comprising of a stimulated echo sequence followed by a train of spin echoes. Figure 3 shows that there is a correlation between the measured (T_1/T_2) ratio and K_{gi}. Rueslåtten et al (1998) has already found a dependency between the (T_1/T_2) ratio and the chlorite content on the surfaces of the porous rock. As the SE-CPMG can be made significantly less time consuming as compared to an inversion recovery experiment, the determination of K_{gi} is a highly competitive alternative to the determination of (T_1/T_2). In addition, the G_i distribution resolves the different sub regions, and K_{gi} yields more information from these regions than a (T_1/T_2) map.

The SE-CPMG method has close resemblance to the diffusion editing sequence by Schlumberger (Hurliman et al (2004)). The major difference is that we acknowledge that the variation in internal magnetic field gradients may be due to both variations in the size of cavities as well as the degree of surface coating on the surface of the porous rock. The K_{gi} parameter aims at normalizing the contribution from various pore sizes (Equation 5), and is a parameter more sensitive to variations in electromagnetic properties at the surfaces of the porous rock. This makes the SE-CPMG method more robust.

REFERENCES

Brownstein K.R. and Tarr C. E. (1979), ”Importance of classical diffusion in NMR studies of water in biological cells”, *Phys. Rev. A*; **19**:2446-53

Drain L.E. (1962), “The broadening of magnetic resonance lines due to field inhomogeneities in powdered samples”, *Proc. Phys. Soc*, **80**

Hürlimann M. et al (2004),”Application of NMR Diffusion Editing as Chlorite Indicator”, *Petrophysics* **45**, 414-421

Rueslåtten H. et al (1998), “NMR studies of an iron-rich sandstone oil reservoir”, *SCA-9821*

Zhang G.Q. and Hirasaki G. J. (2003), “Internal Field Gradients in Porous Media”, *Petrophysics*, **44**, N.6

Zielinski L.J. and Sen P.N. (2003), “Combined effects of diffusion, nonuniform-gradient magnetic fields, and restriction on an arbitrary coherence pathway, *J. Chemical Physics*, **119**, N2,1093-1104