

## Porosity and Pore Size Study by Means of Nuclear Magnetic Resonance and Calorimetry

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**Keywords:** porosity, pore size distribution, NMR, calorimetry

**Abstract:** *The present work involves a comprehensive experimental determination of porosity and pore size distribution in rocks from oil fields formations by Nuclear Magnetic Resonance (NMR) and Differential Thermal Calorimetry (DTC). Both techniques yield complementary results, the DTC measures the amount of heat involved in a phase transition of the sample under study providing bulk information from which the most abundant pore size can be obtained, the NMR allows the determination of the relative pore size distribution very accurately. Both techniques give complementary information to obtain an absolute pore size distribution.*

### Introduction

Nuclear Magnetic Resonance (NMR) as well as Differential Thermal Calorimetry (DTC) have become valuable tools in physics, chemistry, biology and other research fields. Both techniques are widely used as complementary tools in order to obtain a more detailed explanation of the phenomena under study.<sup>1</sup> Nevertheless, both techniques provide information from different scales of interactions. While the NMR arises from the local interaction of the proton magnetic moments with a magnetic field, composed by a constant external magnetic field plus a local field from neighboring magnetic dipoles and paramagnetic impurities, the DTC measures the bulk enthalpy excess of a sample undergoing a phase transition respect to a reference material undergoing the same thermal evolution without any phase change.<sup>2,3</sup>

Petrophysical information, such as porosity, pore size distribution, bound water, and permeability can be obtained from NMR relaxometry.<sup>4</sup> Understanding the principles of NMR relaxation of fluids in rock pores is critical for the correct relaxometry data interpretation. The physical process involves the rotation of the proton magnetization, from its stationary equilibrium state to a direction perpendicular or transverse to the external magnetic field  $B_0$ , followed by the return to equilibrium undergoing two well differentiated relaxation processes. Normally the transverse relaxation, characterized by a time  $T_2$ , dephases the spin magnetization faster than the longitudinal relaxation, characterized by  $T_1$ , process that involves a return to equilibrium by transferring energy from the spins to the surrounding physical system. A well brine saturated rock sample is immersed in an homogeneous magnetic field, which turns out to

have a small gradient due to the natural paramagnetic inhomogeneities of the rock. Therefore the fluid in the pores responds to a spin-echo  $T_2$  experiment with

$$\frac{1}{T_{2\text{surface}}} = \rho \left( \frac{S}{V} \right)_{\text{pore}} \quad (1)$$

$$A(t; C_i, T_{2i}) = \sum_{i=0}^n \left[ C_i \exp\left(-\frac{t}{T_{2i}}\right) - \alpha |C_{i+1} - C_i| \right] \quad (2)$$

with the condition that  $C_{n+1} = 0$ , and where the coefficients  $C_i$  indicate the weight of the decay, providing a means to measure the pore abundance whose sizes are characterized by  $T_{2i}$ , and  $\alpha$  is the regularization coefficient.

The DTC is based on the temperature measurement of two samples, one being the sample under study and the other the reference, undergoing a thermal evolution inside a calorimeter as both gain or loss heat at a given rate. The reference sample is chosen such that it does not have any specific heat anomaly in the temperature range of interest. Any physical change involving a heat evolution of the sample will produce a temperature difference with the reference. A cooling process of a saturated rock will produce a liquid to solid phase transition of the brine inside the pores which in turn produces that its temperature remains constant during the transition. The registered temperature difference, between the rock and the reference, yields a characteristic peak typical of a liquid to solid phase transition.

where the coefficient  $\rho$  is the  $T_2$  surface relaxivity strength of the surface.<sup>4</sup> The most convenient way to measure  $T_2$  is by means of the Carr-Purcell-Meiboom-Gill (CPMG)<sup>2</sup> pulse sequence, which gives the transversal magnetization decay from which the  $T_2$  distribution is obtained taking a discrete non linear regularized Laplace transform,<sup>5</sup> namely the signal amplitude  $A(t; C_i, T_{2i})$  is fit by:

Thus, in a cooling down process the transition temperature depends of the brine salinity and the pore size<sup>6</sup> according to:

$$T_f(a) = \frac{k}{a} + T_f(\infty) \quad , \quad (3)$$

where

$$a = \left( \frac{V}{S} \right)_{\text{pore}} \quad (4)$$

is a measure of the pore size,  $T_f(\infty)$  is the brine fusion temperature corresponding to an infinite pore size. It is convenient to rewrite Ec. (3) in terms of the temperature shift as:

$$\Delta T_f = T_f(a) - T_f(\infty) = \frac{k}{a} \quad (5)$$

Measured values of the constant  $k$  [7] obtained for different compounds are in the range  $4.1 \cdot 10^{-8}$  Km to  $7.3 \cdot 10^{-8}$  K m. Also, studies of samples of controlled pore size<sup>6</sup> yield a value of  $k = 5.7 \cdot 10^{-8}$

K m. It is reasonable to assume an average value of  $k = 5.7 \cdot 10^{-8}$  K m.

Combining equations (1) and (5) follows that the relaxivity constant results:

$$\rho = \frac{k}{T_2 \Delta T_f} = \frac{5.7 \cdot 10^{-8} \text{ K m}}{T_2 \Delta T_f} \quad (6)$$

where  $T_2 = T_{2\text{surface}}$ .

## Materials and Methods

The studied rocks were obtained from geological formations of one prospect oil well of the San Jorge Gulf basin in Argentina. Both rocks are sedimentary sand and its analysis shows that are quite similar although their poral distributions are somewhat different.

These are constituted by friable mature equigranular quartzite without cement with high porosity and permeability to saturation, Table 1.

**Table 1.** Rocks Composition

|      | (%)    |          |           |                        |
|------|--------|----------|-----------|------------------------|
| Rock | Quartz | Feldspar | Moscovite | Ilmenite and magnetite |
| 1    | 95     | 2        | 1         | 2                      |
| 2    | 93     | 3        | 2         | 2                      |

The samples were bottled in such a way that the holder was suitable to perform both NMR and DTC measurements without sample handling. This procedure ensures to keep hydration content of the sample unchanged for long periods of time. The sample holder is made of zirconium oxide allowing good thermal conductivity and very low dielectric properties to radio frequency.

The calorimeter is a standard differential thermal calorimeter specially designed for low temperatures measurements.

The NMR apparatus is a pulsed spectrometer with a working frequency in the range of 2 MHz for protons resonance frequency, and the  $T_2$  measurements were obtained using CPMG pulse sequence with phase alternation. The NMR laboratory, the experimental methods and procedures are ISO 17025:2005 accredited.

## Experimental Results

The temperature differences,  $\Delta T$ , between the samples and the reference versus the evolution time,  $t$ , are depicted in Figs. 1 and 2. The areas under these transition peaks are proportional to the number of water molecules undergoing the transition. The figures also include the transition temperatures of the fusion peaks associated to transitions taking place in sets of pores with different sizes.

The spin-spin relaxation times distributions, namely the weight of the decay,  $C_i$ , versus the corresponding  $T_{2i}$ , are depicted in figures 3 and 4, for rocks 1 and 2. The amplitudes  $C_i$  are related to a characteristic pore abundance, and the relaxation time  $T_{2i}$  to the pore size.

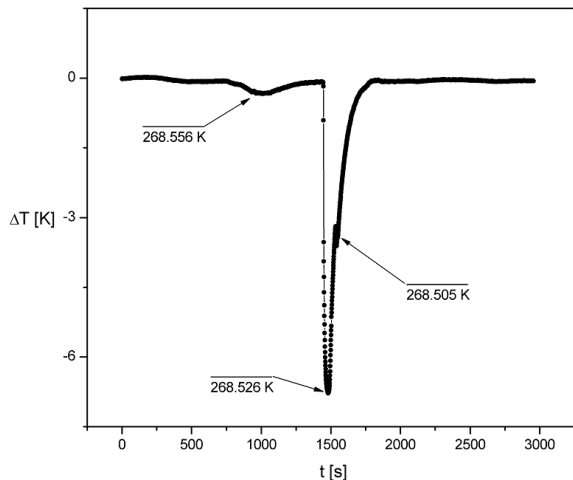


Figure 1. Rock 1,  $\Delta T$  versus time.

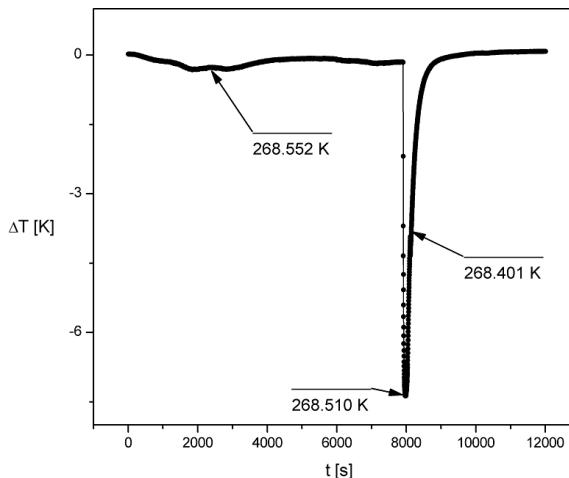


Figure 2. Rock 2,  $\Delta T$  versus time.

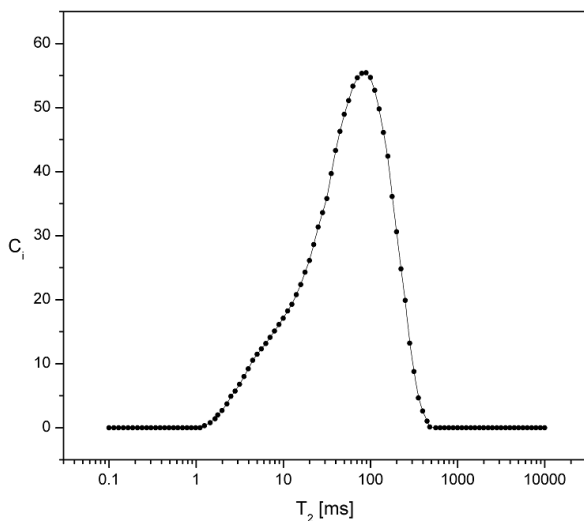


Figure 3. Rock 1,  $C_i$ , pore abundance versus  $T_{2i}$ .

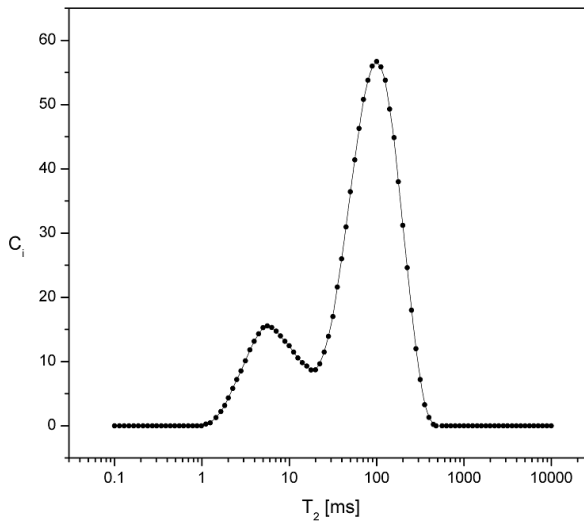


Figure 4. Rock 2,  $C_i$ , pore abundance versus  $T_{2i}$ .

In order to process the NMR and DTC data by means of Ec. 6, it is better to summarize the results for rocks 1 and 2 respectively, Table 2. Where the two peaks in rock 2 at 268.563 K and 268.541 K have been replaced by one at the

average temperature of 268.552 K. The values of  $T_2$  corresponding to the peaks were obtained by fitting the curves, of Figs. 3 and 4, by two lognormal Gaussian distributions.

**Table 2.** Rock 1 and Rock 2 results.

| Roch   | $T_f(\infty)$ | $T_f(a)$  | $\Delta T_f(a)$ | $T_2$                          |
|--------|---------------|-----------|-----------------|--------------------------------|
| Rock 1 | 268.556 K     | 268.526 K | 0.030 K         | $91.6 \cdot 10^{-3} \text{ s}$ |
|        | 268.556 K     | 268.505 K | 0.051 K         | $20.3 \cdot 10^{-3} \text{ s}$ |
| Rock 2 | 268.552 K     | 268.510 K | 0.042 K         | $94.6 \cdot 10^{-3} \text{ s}$ |
|        | 268.552 K     | 268.401 K | 0.151 K         | $6.5 \cdot 10^{-3} \text{ s}$  |

In order to obtain a single valued relaxivity for each rock, we are going to proceed similarly as a  $T_2$  distribution is matched to pore throat size measurements by mercury injection: Namely, the NMR- $T_2$  distribution is shifted until a “good” correlation is obtained with the mercury injection data. This is achieved by shifting the center of mass of  $C_i$  versus  $T_{2i}$  distribution to match the center of mass of the percentage porosity occupied by mercury versus pore throat size distribution. Therefore, in this case, the center of mass of temperature shifts is assigned to the center of mass of the  $C_i$  versus  $T_2$  distribution. Thus, for rocks 1 and 2 respectively:  $T_{2CM}$  (Rock 1) =  $76.5 \cdot 10^{-3} \text{ s}$ ,  $T_{2CM}$  (Rock 2) =  $86.9 \cdot 10^{-3} \text{ s}$ ,  $\Delta T_{CM}$  (Rock 1) = 0.035 K and  $\Delta T_{CM}$  (Rock 2) = 0.045 K.

The  $T_{2CM}$  values are related to the average logarithmic  $T_2$ . Therefore, the results yield values of relaxivity given by:  $\rho(\text{Rock 1}) \cong 21 \cdot 10^{-6} \text{ m s}^{-1}$  and  $\rho(\text{Rock 2}) \cong 15 \cdot 10^{-6} \text{ m s}^{-1}$ .

Considering the errors introduced by the measurements of  $T_2$  and  $\Delta T$ , the relaxivity values have an error of approximately 8%, being the temperature measurements the dominant figure in the error calculation. It is important to remark that the averaged relaxivity used, for these type of rocks, by loggers is approximately  $\rho \cong 15 \cdot 10^{-6} \text{ m s}^{-1}$ .

With the relaxivity results the pore size distribution can be plotted in terms of the pore size. Figures 5 and 6 show the pore distribution in addition to the normalized cumulative integral values which allows to extrapolate the average poral size when it reaches a value of 50. In addition, Fig. 7 shows the absolute cumulative integrals of both rocks, which are related to the rock porosities, and allows to compare the porosities of both rocks.

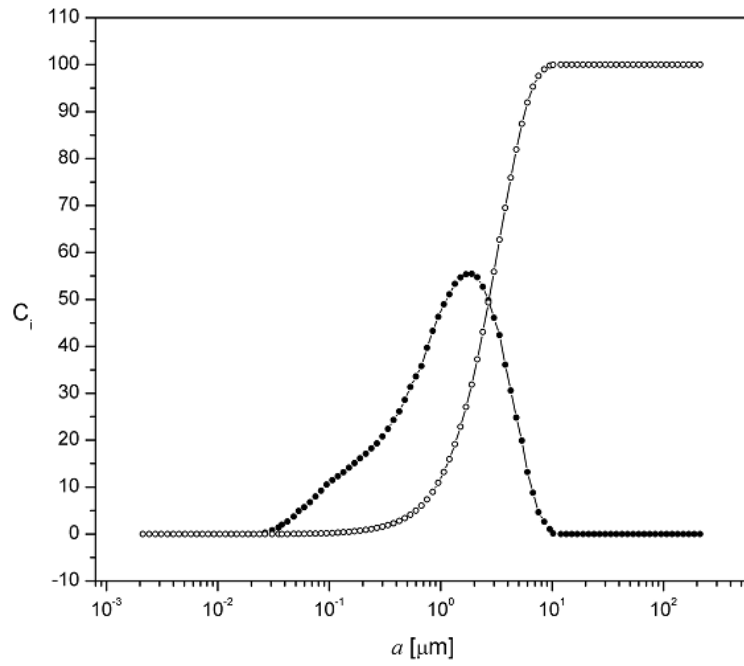


Figure 5. Rock 1,  $C_i$ , pore abundance versus  $a_i$ , and its normalized cumulative integral.

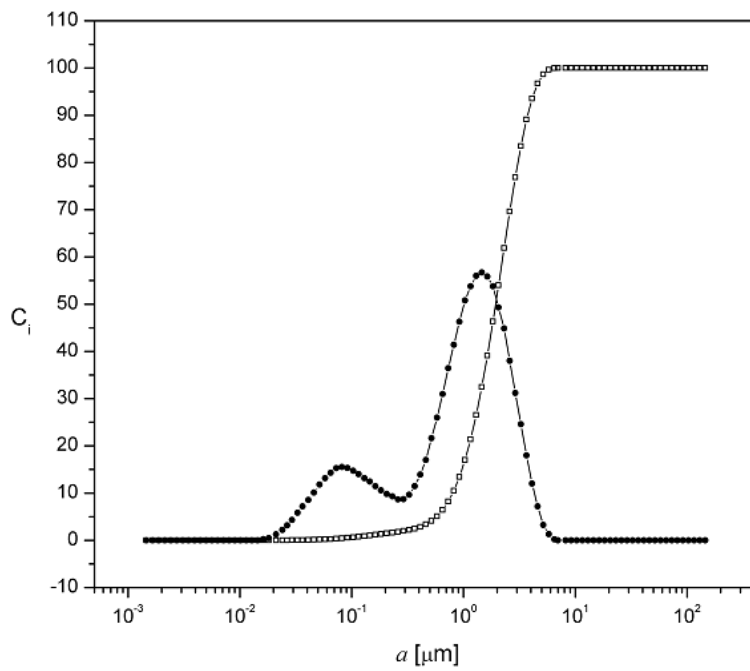


Figure 6. Rock 2,  $C_i$ , pore abundance versus  $a_i$ , and its normalized cumulative integral.

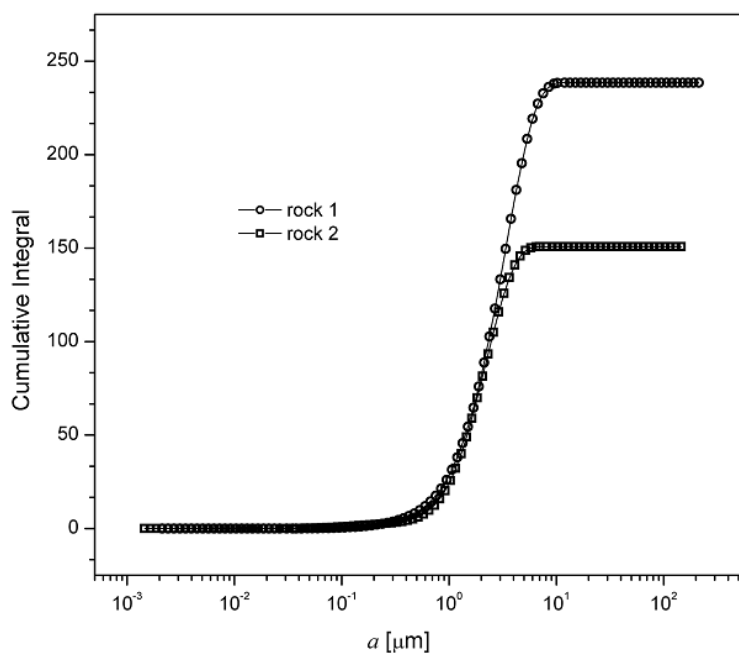


Figure 7. Rocks 1 and 2, cumulative integral versus  $a_i$ .

## Conclusions

Measurements of  $^1\text{H}$  NMR spin-spin relaxation time ( $T_2$ ) of hydrated samples (plugs) and water fusion temperature by DTC, from which the relaxivity factor  $\rho$  was determined. A comparison between the obtained relaxivity factors and the tabulated ones<sup>8</sup>, i.e.  $\rho(\text{sandstone}) \cong 23 \cdot 10^{-6} \text{ m s}^{-1}$ ,  $\rho(\text{dolomite}) \cong 5.4 \cdot 10^{-6} \text{ m s}^{-1}$  and  $\rho(\text{limestone}) \cong 3.2 \cdot 10^{-6} \text{ m s}^{-1}$  shows that even both rocks are constituted quite similar, Table 1, the relaxivity of rock 1 is closer to a sandstone while the relaxivity of rock 2 takes an intermediate value between a sandstone and dolomite.

The combination of these experimental techniques, NMR and DTC, allows an alternative method when mercury injection data are not available. All of these allow us to conclude that the pores size distributions for both plugs were obtained in a fast and neat non destructive procedure which allows the preservation of the samples for other type of measurements.

## Acknowledgements

Financial support was provided by the Universidad Nacional de Córdoba and by the Consejo Nacional de Investigaciones Científicas y Técnicas (through grant PIP 02588). The company MR Technologies S.A. provided the samples. All are gratefully acknowledged.

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