[PS]NMR Cryoporometry: An Alternate Non-Destructive Technique for the Measurement of Pore Size Distribution in Shales*

Marc Fleury[1] and Eric Kohler[1]

Search and Discovery Article #41951 (2016)**
Posted November 28, 2016

*Adapted from poster presentation given at AAPG Annual Convention & Exhibition, Calgary, Alberta, Canada, June 19-22, 2016

[1]IFPEN, Rueil-Malmaison, France (marc.fleury@ifpen.fr)

Abstract

The characterization of shales is challenging due to their very small pore sizes. In many previous works, we have shown that Nuclear Magnetic Resonance (NMR) relaxation techniques are well suited for detecting and quantifying water in nanopores. However, the usual T2 distribution of relaxation times does not necessarily represent the true distribution of pore sizes in nanoporous samples due to diffusive exchanges between pores, yielding apparent narrow pore size distribution. The NMR cryoporometry experiment relies on the shift of the melting temperature of the saturating liquid, which is itself a function of pore size according to Gibbs-Thomson theory. In practice, a sample (a cylinder of diameter 4 mm and length 20 mm) saturated with water is rapidly frozen at about -30° C and then heated slowly while the amount of water melted at a given temperature is measured by NMR. Typically the range that can be explored lies between 2 nm and 1 micron, well suited for the study of shales. Importantly outside this range, the pore volume can be determined but a pore size cannot be associated with this volume. We used this technique on different shales from different origins and compared the results with other techniques such as NMR T2 distribution, high pressure mercury injection and nitrogen adsorption. The measured distributions can differ significantly and we discuss the various physical reasons behind. The NMR cryoporometry technique open new horizons for characterizing shales in their natural hydrated state.

NMR cryoporometry: an alternate non-destructive technique for the measurement of pore size distribution in shales.

M. FLEURY , E. KOHLER
IFP Energies nouvelles, Rueil-Malmaison, France

Motivations

The characterization of shales is challenging due to their very small pore sizes. In previous works, we have shown that Nuclear Magnetic Resonance (NMR) relaxation techniques are well suited for detecting and quantifying water in nanopores. Existing techniques, including NMR T_2, have several drawbacks:

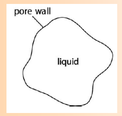
Mercury intrusion	Need a dry sample , Destructive , > 4 nm
N_2 adsorption	Need a dry sample < 100 nm
Thermoporometry (DSC)	Similar to NMR cryoporometry
NMR relaxation	Need calibration – pore coupling
Imaging (FIB, SEM, TEM…..)	Resolution – field of view compromise

NMR cryoporometry: principle

The melting point depression T_m of a confined liquid depends on the pore size (Gibbs-Thomson equation)

$$\Delta T_m(x) = T_m^{Bulk} - T_m(x) = \frac{k_{GT}}{x}$$

T_m^{Bulk} : Bulk Melting Temperature
x : pore size
k_{GT} : Gibbs- Thomson constant



Pore size distribution:

V: volume of liquid

Pore size x: curvature dV/dS of a pore of volume V and surface S

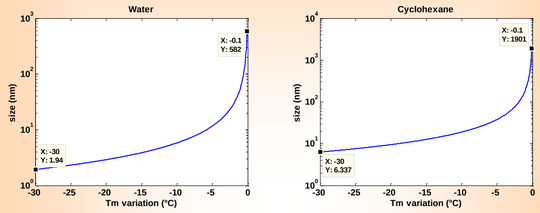
$$\frac{dv}{dx} = \frac{dv}{dT}\frac{dT}{dx} = -\frac{k_{GT}}{x^2}\cdot\frac{dv}{dT}$$

At a given temperature below zero, small pores still contain liquid water instead of ice

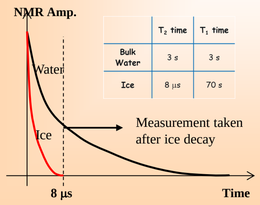
Range of pore size: 2 nm up to 500 nm with water, 6nm up 2 µm with cyclohexane. Pore volumes outside these ranges can be determined to obtain total porosity.

Shift of melting temperature

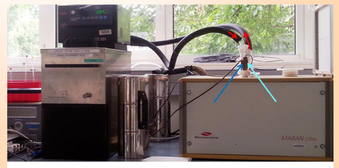
k_{GT}=58.2 K.nm $\quad \Delta T_m(x) = \frac{k_{GT}}{x}$ $\quad k_{GT}$=190.1 K.nm



Direct detection and quantification of the amount of liquid with NMR:
Very short relaxation of ice compared to water → liquide volume can be measured directly

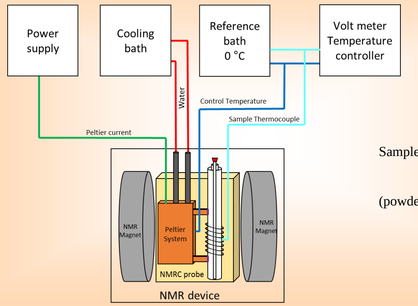


	T_2 time	T_1 time
Bulk Water	3 s	3 s
Ice	8 µs	70 s



Experimental set-up

Special probe inside a standard low field NMR set-up
Temperatures regulated and controled wih a Peltier system (sensitivity 0.01°C)

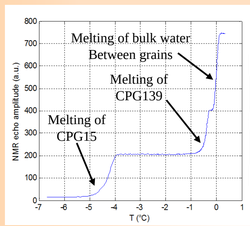


Sample size: D=4mm
L<20mm
(powder or cylinder)

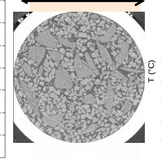
Tests

Test sample: mixture of calibrated porous glass (CPG)
Porous glasses with cylindrical pores with 2 diameters: 15 nm (CPG15) and 139 nm (CPG139).

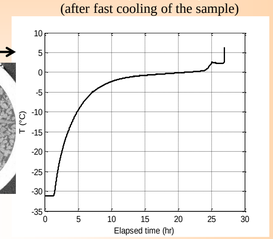
Raw signal



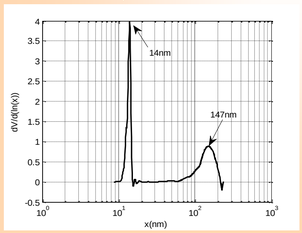
4 mm



Applied temperature ramp (after fast cooling of the sample)



Derivative/normalization



Derived quantities from NMR cryoporometry in agreement with weight

NMR T_2 quantification not accurate due to diffusive pore coupling

Method	*15 nm*	*139nm*	*Inter-granular +bulk*
Weight	27.0	27.3	45.6
Cryoporometry	26.0	27.0	47.0
T_2 Relaxation	21.5	88.5	
T_2 Relaxation at -0.15° C	28.4	24.6	-

References

M. Fleury, E. Kohler, F. Norrant, S. Gautier, J. M'Hamdi, L. Barré, Characterization and Quantification of Water in Smectites with Low-Field NMR, J. Phys. Chem. C. 117 (2013) 4551–4560.

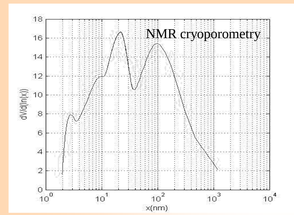
M. Fleury, R. Fabre, J.B.W. Webber, Comparison of pore size distribution by NMR relaxation and NMR cryoporometry, Proceeding of the Society of Core Analysts Annual Meeting (2015).

J. Mitchell, J. Webber, J. Strange, Nuclear magnetic resonance cryoporometry, Phys. Rep. 461 (2008) 1–36.

Song, Yang; Davy, C. A.; Troadec, D.; Blanchenet, A.-M.; Skoczylas, F.; Talandier, J.; Robinet, J. C. (2015) Multi-scale pore structure of COx claystone: Towards the prediction of fluid transport. In : Marine and Petroleum Geology, vol. 65.

Shale samples

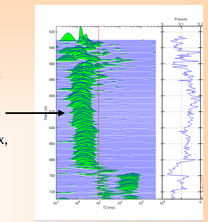
Caprock sample: Callovo-Oxfordian formation, porosity 14.8%, water permeability 7.3 nD (1 nD=10^{-21} m^2)

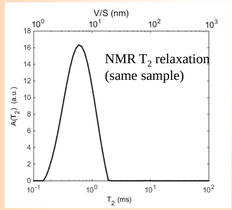


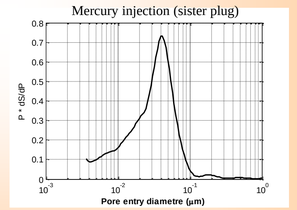
Sample taken at depth 604m

Well EST 433

Montier sur Saulx, France





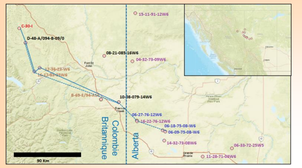


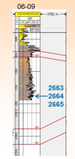
Pore size distribution in qualitative agreement with published data (imaging, Song et al. 2015)

NMR T_2 distribution → narrow distribution due to pore coupling effect (averaging effect)

Difference with mercury injection → throat size instead pore size, percolation issue

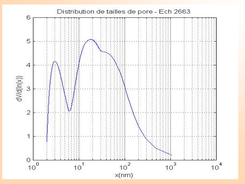
Sample from Montney (porosity 3%)

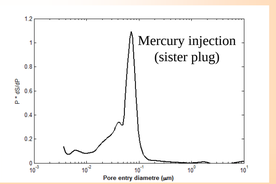




Sample 2663 from well 06-09

at 2139.8 m





Conclusion

The NMR cryoporometry technique is well suited to measure pore size distribution for water saturated samples in the range 2 nm up to 500 nm. Pore volumes outside this range can be measured to obtain total porosity. The typical duration of the experiment is 24 hours. For pore sizes smaller than about 500 nm, NMR T_2 distribution are not representative of pore size distribution due to pore coupling effects.

To perform cryoporometry, a specific NMR probe is required and can be installed in standard NMR low-field apparatus.

Contact: marc.fleury@ifp.fr