Different techniques to quantify pore-space lengths in porous rocks and artificial porous media

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Pore-size dimensions and *distributions* and *pore-space connectivity* have, in general, influence on fluid transport within a porous structure. Porous media are routinely characterized by techniques such as gas adsorption and mercury porosimetry, as well as by NMR methods. The results depend strongly on the length scales involved. Only simplified geometrical representations of the pore space (e.g. a bundle of capillary tubes) can currently easily be modelled. Such pore network models can be used to predict macroscopic transport coefficients that can then be compared with experimental values. However, a fundamental understanding of how local microstructural variations can influence macroscopic transport is still lacking, and it is in this regard that NMR techniques have considerable potential. Complementary experiments can provide more information on the pore structure than a single technique alone. In this paper we focus on the NMR methods of Relaxometry (MRR) and imaging and their validation and inter-relation using Mercury Porosimetry (MIP) and optical scanning (SEM), in natural and artificial systems, such as rocks and fired ceramics [1]. Relaxation measurements in rock samples and ceramic mixtures have been compared with Hg-injection porosimetry measurements. The two methods show both points of agreement and of difference owing to different operational definitions of the characteristic dimensions investigated, i.e pore body and pore throat sizes.

EXPERIMENT

SAMPLES. Ceramic samples analysed in this study were obtained processing a body mix, based on K-feldspar and Na-feldspar, used for porcelain stoneware tile and fired at 1280°C for three different firing times: 0, 10 and 20 minutes. The sintered samples were respectively labelled A, B and C. The composition of the samples is clay1 (10,0%), clay2 (38,6%), K feldspar (5,6%) and Na feldspar (35,5%). Rocks: marble, sandstone (Firenzuola) and limestone (Pietra di Lecce).

NMR MEASUREMENTS. MRI measurement were performed at 30°C by an ARTOSCAN (Esaote SPA, Genova, Italy), a tomograph consisting of a 0.2 permanent magnet (15 mT/m maximum gradient intensity), corresponding to 8 MHz for ^{1}H. Axial sections were acquired by multislice spin echo sequence with echo time TE = 10 ms and repetition time TR = 700 ms.

^{1}H longitudinal relaxation curves were obtained through inversion-recovery (IR) pulse sequence (π-t-π/2-acquisition) at 25°C and 20 MHz by a homemade relaxometer with a SPINMASTER console (Stelar, Mede, PV). ^{1}H transverse relaxation curves were obtained by Carr-Purcell-Meiboom-Gill (CPMG) pulse sequences. Quasi continuous distributions have been computed by UPEN.

sample	diameter (cm)	height (cm)	mass of water saturating the sample (g)	Φ (%)	use
A	3.895	0.554	0.1276	17.0	Imaging
B	3.760	0.525	0.2572	4.4	Imaging
C	3.740	0.510	0.0089	0.2	Imaging
A'	0.763	0.550	0.0431	17.2	Relaxometry
B'	0.772	0.512	0.0133	5.5	Relaxometry
B''	0.696	0.519	0.0082	3.8	Relaxometry
C'	0.770	0.487	0.0005	0.2	Relaxometry

CONVENTIONAL ANALYSES

A detailed analysis of the microstructure of the samples was carried out using SEM (JEOL T330, Japan) and mercury intrusion porosimetry (Porosimeter 2000, Fisons). SEM gives pore sizes and the morphology of the bulk and surface of the samples, and MIP gives the porosity and the pore throat size distribution.

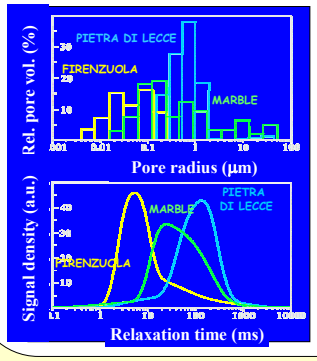
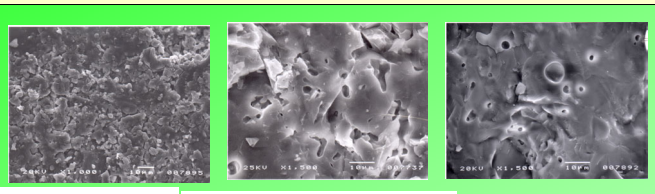


Fig1

COMPARISON BETWEEN SEM, MIP AND MRR RESULTS in natural and artificial systems

Fig1. Both the shape and the peak position of the pore size distributions of the investigate natural systems (*Pietra di Lecce, Marble, Firenzuola*) correlate well in the different scales referring to MRR and MIP [2]. On the contrary, ceramic samples show pore size distributions from MRR that do not fit with those from MIP. We observed changes of the pore space structure in ceramics following the sintering process, taking place holding samples at fixed maximum firing temperature of 1280°C for different length of time Both SEM and NMR **(fig. 2,4)** show an increase in pore size with the soaking time (time of permanence at a fixed firing temperature). NMR imaging (images not reported) and SEM also reflect inhomogeneity on the sample size scale in the sample with intermediate soaking time. The discrepancy between pore and pore-channel sizes **(fig 3,4)** increases with the soaking time and makes it clear that a higher level of sintering allows the formation of larger pores connected by smaller channels. For the longest soaking time sample, the SEM images and the lack of a NMR signal make it clear that there is substantial isolated porosity and essentially no connected porosity.

Fig2. Scanning electron microscopy images of samples A, B and C, from left to right, corresponding to 0, 10, 20 min soaking time respectively. Marker = 10 μm. There is substantial porosity in sample C, even though NMR and porosity measurements show that there is not significant *connected* porosity.



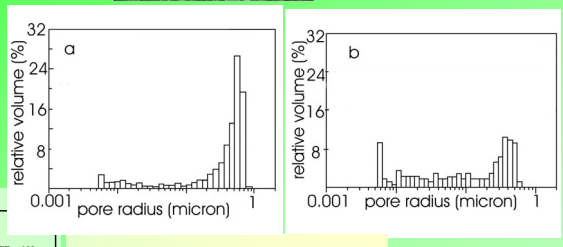


Fig3a,b. Distributions of the pore volume as function of the pore *channel* (or pore throat) *radius* measured by mercury intrusion porosimetry. (a) sample A' (0 min soaking time); (b) sample B' (10 minutes soaking time). These are the same A' and B' samples used for the relaxation measurements. Most pore space in A' is fed by pore channels, or throats, near the maximum size, while much of the pore space of B' is fed by channels with a wide range of size.

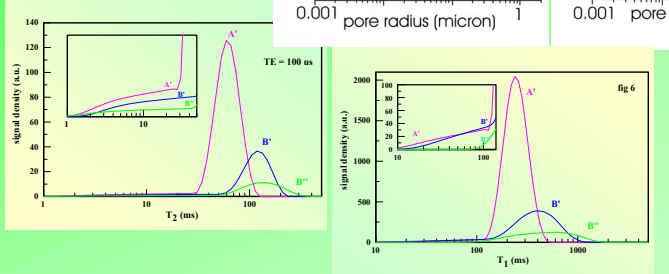


Fig4. Distributions of relaxation times. The curves in the graph on the left are for T_2 with TE= 100 μs, and the curves on the right are for T_1. In each case the highest peak is for A' (0 min soaking time), the next for B' and the lowest for B''. Samples B' and B'' were both cored from B (10 min soaking time). The insets show details of the tails for short times.

REFERENCES

[1] P. Fantazzini, A. Salem, G. Timellini, A. Tucci, R.Viola, J. Appl. Phys., 94:5337-5342 (2003).

[2] Borgia G.C, Bortolotti V., Camaiti M., Cerri F., Fantazzini P., Viola R. In *La comunicazione multimediale per i beni culturali.* M.Rossi and P.Salonia eds., Addison Wesley (2003).

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