

● *Contributed Paper***WATER ABSORPTION IN MORTAR DETERMINED BY NMR**

L. PEL,* K. HAZRATI,† K. KOPINGA,* AND J. MARCHAND†

*Department of Physics, Eindhoven University of Technology, P.O. Box 513, Eindhoven, The Netherlands; and †Concrete Canada and Center de Recherche Interuniversitaire sur le Béton, Université Laval, Sainte-Foy, Québec, Canada

Nuclear magnetic resonance (NMR) offers the possibility to determine moisture profiles in porous building materials. Moreover, the relaxation of the nuclear magnetic resonance signal can provide additional information on the water distribution in the microstructure. For mortar, it is shown that the transverse relaxation yields information on the distribution of water in the gel pores and capillary pores. Moisture profiles and relaxation were measured during water absorption. The effect of the drying treatment on the microstructure and the water absorption was investigated. © 1998 Elsevier Science Inc.

Keywords: NMR; Water absorption; Mortar; T_2 relaxation.

INTRODUCTION

Moisture in porous materials can give rise to several kinds of damage, e.g., frost damage, ion uptake and corrosion. Therefore, a detailed knowledge of the moisture transport is essential for understanding the durability of these materials. This research project mainly focuses on the water transport by capillary absorption in dry mortars. These mortar samples were made with white cement containing low amounts of magnetic oxides ($\text{Fe}_2\text{O}_3 \sim 0.3\%$ and $\text{Mn}_2\text{O}_3 \sim 0.03\%$) and 50% (in volume) siliceous sand. The samples with various water-to-cement ratios were allowed to cure in a saturated lime solution for at least 1 year. Special attention was given to the preparation of dry samples for the absorption experiments. Direct oven drying at 105°C of saturated samples is a common preparation technique. This severe drying may, however, cause a general coarsening of the pore structure, due to the high internal stresses exerted on the fragile components of the paste by the receding water menisci. First exchanging the pore water with a miscible, low-surface-tension fluid (in this case, propan-2-ol) and then slowly drying at 40°C and 105°C may cause less alternation to the microstructure.¹ These respective techniques will be abbreviated as oven and propanol dried. Absorption experiments were performed on oven- and propanol-dried samples of the same composition (water-to-cement ratio).

The mathematical formulation of mass transfer at the macroscopic level in porous media is usually based on diffusion equations first formulated by Philip and de Vries.² A more fundamental basis for these equations was given by Withaker³ and Bear.⁴ If the gravity is neglected, the liquid moisture transport for the one-dimensional isothermal problem considered in this paper can be described by a non-linear diffusion equation:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x} \left(D_\theta \frac{\partial \theta}{\partial x} \right). \quad (1)$$

In this equation, θ [$\text{m}^3 \text{m}^{-3}$] is the volumetric liquid moisture content and D_θ [$\text{m}^2 \text{s}^{-1}$] is the moisture diffusivity, which is a function of the actual moisture content.

MATERIALS AND METHODS

For the experiments described here, a home-built nuclear magnetic resonance (NMR) apparatus was used, which operates at a frequency of 34 MHz ($B_0 = 0.8$ T) and was specially designed for quantitative measurements in porous materials with short nuclear relaxation times. An extensive description of this NMR apparatus can be found in Ref. 5 and 6.

The mortar samples used in the experiments are cylindrical rods with a diameter of 20 mm and a length of

Address correspondence to Dr. L. Pel, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The

Netherlands. E-mail: l.pel@phys.tue.nl

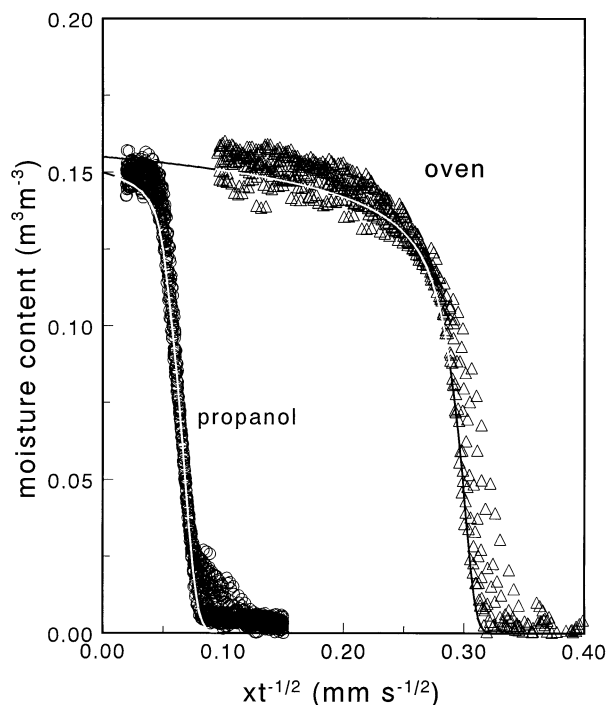


Fig. 1. Boltzmann transform of the measured moisture profiles for the two types of mortar: oven dried (Δ) and propanol dried (\circ). (—) Boltzmann transform of the moisture profiles that were numerically simulated based on the moisture diffusivity approximated by two exponential functions (see Table 1).

40 mm. Because our aim was to perform quantitative measurements, special attention was given to the impedance matching of the NMR probe. To reduce the effects of the variation of the dielectric permittivity by a changing moisture content in the sample, a Faraday shield was placed between the tuned circuit ($Q \approx 40$) of the probe head and the sample. Anderson gradient coils were employed, and yielded magnetic field gradients in the vertical direction up to 0.3 T/m. No attempts were made to switch these gradients during the individual spin-echo sequences. The one-dimensional spatial resolution of the equipment was found to range between 0.8 and 1.0 mm.⁵ The moisture profiles are measured using frequency scans over approximately 400 KHz.

Moisture Profiles

First, the moisture profiles were measured during absorption for both oven-dried and propanol-dried samples. These samples were allowed to freely absorb water through one end. In case of absorption, all measured profiles for one material can be related by the Boltzmann transformation, $\lambda = x t^{-1/2}$ (e.g., see Ref. 6). In Fig. 1 the Boltzmann-transformed profiles are plotted for one type of mortar (water-to-cement ratio = 0.40), both oven and

Table 1. The coefficients of the exponential function $D_\theta = D_0 \exp \beta\theta$, describing the moisture diffusivity for absorption, and the capillary moisture content θ_{cap} .

Material		D_θ [$\text{m}^2 \text{s}^{-1}$]	β [—]	θ_{cap} [$\text{m}^3 \text{m}^{-3}$]
Oven	$\theta < 0.126$	5×10^{-10}	25.3	
dried	$\theta > 0.126$	1×10^{-14}	115.1	0.155
Propanol	$\theta < 0.135$	2×10^{-10}	17.3	
dried	$\theta > 0.135$	1×10^{-21}	208.4	0.15

propanol dried. In both cases, the transformation yields a distinct curve on which the data from the various profiles collapse. This indicates that the moisture diffusivity does not depend on the position in the sample and supports the modeling of the moisture transport during water absorption by a diffusion equation. For both materials a sharp wetting front is observed. It can be seen that the water penetration factor (position of the wetting front divided by \sqrt{t}) for the oven-dried sample is about a factor 4 higher than for the propanol-dried sample. This indicates that indeed during the oven drying a continuous network of larger pores is formed, resulting in a higher absorption rate. Also in Fig. 1 computer simulations are given of the water transport based on an approximation of the moisture diffusivity by two exponential functions of which the coefficients are given in Table 1.

Relaxation Measurements

The relaxation of the NMR signal can provide additional information on the water distribution in the microstructure. According to the fast exchange theory, the transverse relaxation time in a spherical pore, neglecting the bulk liquid relaxation, is given by a single exponential decay with a relaxation time T_2 .^{7,8}

$$T_2 = \frac{T_{2s} a}{\lambda/3}. \quad (2)$$

Here T_{2s} is the surface relaxation time, λ is the thickness of the surface layer, which will be taken equal to 3 \AA ,⁸ and a is the pore radius. For other pore geometries, the proportionality constant $a/3$ may be slightly different (e.g., $a/2$ for cylinders). The surface relaxation was determined for various mortar samples of different water-to-cement ratios, both oven and propanol dried. These measurements were done by putting initially dry samples in an atmosphere with a controlled relative humidity. This humidity was increased slowly until a small NMR signal developed, which is attributed to water present at the surface of the pores. In a large humidity range, the signal shows a mono-exponential relaxation with a constant value of T_2 , which is associated with T_{2s}

in Eq. (2). From these measurements, a surface relaxation time $T_{2s} = 85 \pm 15 \mu\text{s}$ was found. (J.Y. Jehng⁷ reported a T_{2s} of $60 \mu\text{s}$ for his hydrated mortar samples).

For saturated mortar samples, a clear two-exponential decay is found. This can be understood from the structure of mortar. Mortar consists of three components:⁹ 1) Unhydrated cement grains; 2) hydrated products containing so-called gel-pores which grow around the cement grains. These gel pores are of the order of $5\text{--}100 \text{ \AA}$; 3) Capillary pores, which are the remnant of the water-filled space between the hydrating grains. These capillary pores have dimensions of the order of $0.01\text{--}10 \mu\text{m}$. This pronounced bimodal pore distribution is reflected in the relaxation as a two exponential decay. Therefore, a double exponential decay was fitted to the data:

$$\theta_{\text{total}} \frac{S(t)}{S(0)} = \theta_{\text{gel}} e^{-\frac{t}{T_{2,\text{gel}}}} + \theta_{\text{cap}} e^{-\frac{t}{T_{2,\text{cap}}}} \quad (3)$$

Here $S(t)$ is the spin-echo signal intensity at echo time t , θ_{total} is the total volumetric liquid moisture content, θ_{gel} and θ_{cap} are the volumetric moisture contents in the gel and the capillary pores, $T_{2,\text{gel}}$ and $T_{2,\text{cap}}$ are the relaxation times of the gel and capillary pores. The fitted values of T_2 were converted into pore sizes using Eq. (2) and the value of T_{2s} mentioned above.

For saturated samples, both oven and propanol dried, gel pores are found with dimensions of the order of 25 \AA . However, for the capillary pores it is found that the pores of the oven-dried sample are of the order of $0.035 \mu\text{m}$, which is almost twice the pore size of the propanol-dried sample, which is of the order of $0.015 \mu\text{m}$. A clear difference in the percentage liquid in the capillary pores is found: 60% for the oven-dried and 35% for the propanol-dried sample. These results correspond well to independent mercury intrusion porosimetry and water vapour desorption measurements.¹⁰ The larger capillary pores for the oven-dried sample are clearly reflected in the water absorption experiments plotted in Fig. 1.

To get some additional information on the water distribution during absorption, the relaxation was measured continuously at one position, i.e., 12.5 mm from the bottom of the sample, in an absorption experiment that lasted 48 h. The resulting relaxation times, obtained by fits of the data with a double-exponential function, Eq. (3), are given in Fig. 2. The passage of the front after about 1 h can be clearly identified. From the time dependence of $T_{2,\text{cap}}$ it can be seen that the larger capillary pores are filled as the front passes first. The subsequent decrease of $T_{2,\text{cap}}$ indicates that gradually smaller pores are filled, resulting in a decreasing average pore size. This effect is very pronounced for the oven-dried sample.

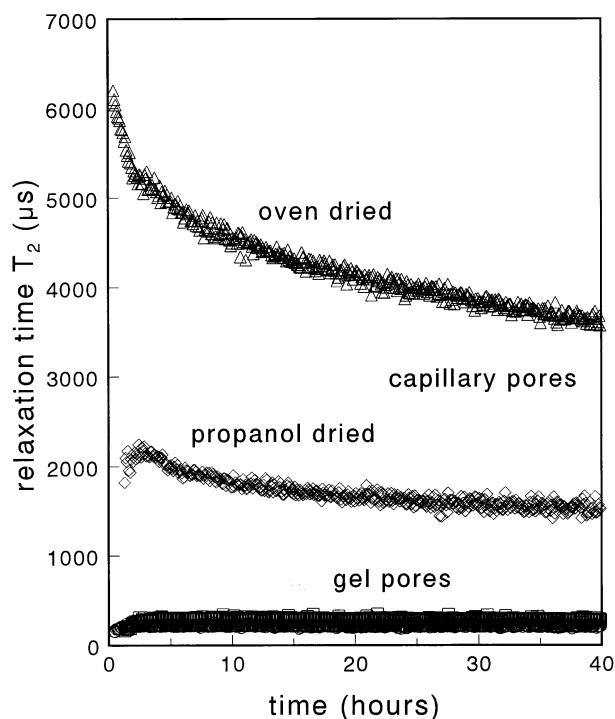


Fig. 2. The time dependence of $T_{2,\text{gel}}$ and $T_{2,\text{cap}}$ for an oven- and propanol-dried mortar sample obtained by fitting a double-exponential decay to the relaxation measurements during water absorption.

CONCLUSIONS

The water absorption in mortar samples can be described by a non-linear diffusion equation. The preparation of the dry samples, oven dried or propanol dried, has a large influence on the microstructure. The NMR measurements show a double exponential decay of the transverse magnetization which reflects the bimodal pore sizes, gel and capillary pores. These measurements also show that pores collapse during oven drying, resulting in a larger fraction of capillary pores. Therefore, oven-dried samples have a faster water absorption than propanol-dried samples.

Acknowledgments—Part of this project was supported by the Dutch Technology Foundation (S.T.W.).

REFERENCES

1. Feldman, R.F. Effect of pre-drying on the rate of water replacement from cement paste by propan-2-ol. II Cemento 3: 193–201; 1988.
2. Philip, J.R.; de Vries, D.A. Moisture movement in porous materials under temperature gradients. Trans. Am. Geophys. Un. 38: 222–232; 1957.
3. Whitaker, S. Simultaneous heat, mass and momentum transfer in porous media: A theory of drying porous media. Adv. Heat Transfer 13: 119–200; 1977.

4. Bear, J.; Bachmat, Y. Introduction to Modeling of Transport Phenomena in Porous Media, Vol. 4. The Netherlands: Kluwer, Dordrecht; 1990.
5. Kopinga, K.; Pel, L. One-dimensional scanning of moisture in porous materials with NMR. *Rev. Sci. Instrum.* 65: 3673–3681; 1994.
6. Pel, L. Moisture transport in porous building materials. Ph.D. thesis. The Netherlands: Eindhoven University of Technology; 1995.
7. Jehng, J.Y. Microstructure of wet cement pastes: a nuclear magnetic resonance study. Ph.D. thesis. Chicago: Northwestern University; 1995.
8. Halperin, W.P.; D'Orazio, F.; Bhattacharja, S.; Tarczon, J.C. Magnetic Resonance relaxation analysis of porous media. In: J. Klafter, J.M. Drake (Eds). *Molecular Dynamic in Restricted Geometries*. New York: John Wiley and Sons, 1989; pp. 311–350.
9. Powers, T.C.; Brownnyards, T.L. Studies of the Physical Properties of Hardened Cement Paste, Bulletin 22. Research Laboratories of the Portland Cement Association. Chicago: Portland Cement Association; 1948.
10. Hazrati, K. Étude des mécanismes de transport de l'eau par absorption capillaire dans des matériaux cimentaires de haute performance. Ph.D. thesis. Canada: Laval University; 1998.