Microporous and Mesoporous Materials 139 (2011) 16–24

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Application of ^{1}H NMR to hydration and porosity studies of lime–pozzolan mixtures

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ARTICLE INFO

Article history:
Received 18 July 2010
Received in revised form 9 October 2010
Accepted 10 October 2010
Available online 16 October 2010

Keywords:
NMR relaxometry
Mercury porosimetry
Nitrogen adsorption
Porosity
Mortar hydration

ABSTRACT

^{1}H nuclear magnetic resonance (NMR) relaxation is applied to lime–pozzolan mixtures to monitor in real-time the hydration and porosity evolution during setting. The hydrated products formed during the setting of these mixtures are similar to those formed in hydraulic binders (e.g. cement and natural hydraulic limes). In this work, we demonstrate that by using a portable, low field (0.29 T) Halbach magnet it is possible to study in detail, the evolution of the pore structure, modified through the formation of C–S–H and C–A–H, by means of the ^{1}H NMR technique. Contrary to the standard porosimetry methods, which require drying procedures before analysis, NMR is a non-invasive straightforward technique, allowing the study of the hydration kinetics in real-time, during the setting and hardening of the lime–pozzolan binding system. Thus, by measuring the ^{1}H NMR spin–lattice relaxation T_1 of two lime–pozzolan mixtures, it was possible to distinguish between different pore populations within the system (at different setting periods), and to study the growth of the hydrated phases. The interpretation of the results proved that, similarly to mercury intrusion porosimetry (MIP) and nitrogen adsorption, ^{1}H NMR probes the development of the pore structure within the lime–pozzolanmortar matrix, indicating key changes of pore size populations.

1. Introduction

The simultaneous monitoring of hydration and porosity evolution in freshly synthesized mortars is a key issue for assessing their performance and adjusting their compositional and curing parameters. In the case of conservation mortars for archaeological and architectural heritage, the performance requirements are variable and specific for each monument. At the same time, due to the nature of these structures, there is a need for continuous but non-invasive monitoring of the mortar hardening process, through the recording of parameters that control it, such as hydration and porosity.

During the setting and hardening processes of lime–pozzolan mortars, which are strongly affected by the presence of water [1], various physical and chemical phenomena occur, which modify their microstructure. The setting reactions that take place during their hardening result in the formation of a variety of calcium silicate (C–S–H) and calcium aluminate hydrated (C–A–H) phases [2], which grow within the pore space of the mixtures and modify their initial pore space characteristics (open porosity, pore-size distribution and specific surface area). It is, therefore, clear that hydration reactions and pore space characteristics are directly interrelated and are responsible for the gradual strengthening of the mortar mixtures [3,4].

Several methods are currently available for determining the pore structure of porous materials [5,6]. Most of them are invasive, as they involve sampling and an hydration – stop process, which affects the amount and the type of the hydrates present in the paste [7] and consequently the pore – space properties of the mixtures. In contrast, nuclear magnetic resonance (NMR) is a fast, potentially non-invasive, technique, for the characterization of the internal structure of a porous material, based on its mobile water molecule content [8].

Over the years, NMR has managed to successfully provide valuable information about porosity, pore-size distributions and the hydration kinetics, especially in cement based materials [9–14]. This technique has the advantage of the nuclear-spin selectivity, where only one nuclear – spin isotope is detected at a time, providing information in real-time, even the earliest few minutes. The successful application of ^{1}H NMR relaxometry to the study of the microstructure development in cement pastes provides the

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doi:10.1016/j.micromeso.2010.10.010

necessary background for the application of the technique to similar materials. In this context, the present work deals with the application of ^{1}H NMR relaxometry, to continuously follow and interpret the hydration and porosity evolution in a lime – natural pozzolan system. The method was applied to two mixtures, consisting of two different amounts of pozzolan powder with the same kneading water.

The selection of the specific type of mortar was based on the fact that lime–pozzolan mortars have been widely used, since antiquity, as a multi-purpose building material, exhibiting remarkable performance over time [15,16]. In addition, traditional building materials and techniques are seeing in revival lately aimed at reducing energy consumption, CO_2 and particulate matter emissions [17,18] for the construction of buildings and the restoration of architectural monuments, leading to renewed interest in the use of lime–pozzolan binders [19,20].

In the work presented here, ^{1}H NMR T_1 distribution profiles, attributed to mobile water molecules in lime – pozzolan pastes, as a function of hydration time, are obtained and modeled to describe the pore distribution. The results were compared and correlated to pore-size distributions obtained by conventional MIP and nitrogen adsorption. The T_1 relaxation measurements were carried out in a portable lightweight permanent Halbach magnet, with a low static magnetic field $B_o = 0.29$ T. Data analysis was performed by using an inverse Laplace transform, which leads to T_1 distribution profiles, clearly demonstrating the development of porosity and the formation of two distinct pore populations. In conjunction with ^{1}H NMR, MIP and nitrogen adsorption, microstructural parameters were studied by scanning electron microscopy (SEM).

1.1. NMR relaxation in porous materials

Lime – pozzolan mixtures are characterized as hydraulic binders hardening through a hydration mechanism. Compared to cements, they have a considerably slower hydration rate and develop a higher porosity matrix [21,22].

The pore-size distributions in cement systems have been successfully determined using NMR spin–lattice relaxation measurements [23–27], where the relationship between T_1 and the pore size is based on the fast-exchange relaxation theory [28]. In principle, the T_1 of a fluid (typically water) confined within a pore, can be used to determine the pore diameter (actually, the ratio of pore volume to surface area). The presence of the pore wall increases the relaxation rate and thus, for a given material, T_1 will decrease as the pore size decreases [24,29].

In particular, it is well known that the relaxation rate, $1/T_1$, of mobile water molecules is enhanced near a liquid–solid interface. This is due to the exchange between the free and bonded water and the presence of paramagnetic sites on the solid surface [30]. In the fast-exchange limit the overall spin–lattice rate within a given pore is expressed as:

$$\frac{1}{T_1} = \frac{1-\eta}{T_{1(bulk)}} + \frac{\eta}{T_{1(surf)}} \tag{1}$$

where $1/T_{1(surf)}$ is the surface relaxation rate of the water adsorbed at the pore surface, $1/T_{1(bulk)}$ is the free water relaxation rate and η is the fraction of adsorbed water molecules at the pore surface [31,32]. As, $1/T_{1(bulk)}$ is negligible compared to the rate of relaxation at the pore surface $1/T_{1(surf)}$, the overall spin–lattice $(1/T_1)$ rate within a spherical pore filled with water, with volume V and surface S is expressed as [31,32] $1/T_1 = (1/T_{1(surf)})(\varepsilon S/V)$, where ε is the thickness of the water layer at the pore surface and S/V is the pore surface to volume ratio.

Thus, the overall relaxation rate depends linearly on the S/V ratio of the pores. As a consequence, in complex porous materials such as lime–pozzolan systems, with pore sizes extending from nanometers to micrometers, T_1 is spread over a wide distribution of relaxation times, which directly reflect the complex pore microstructure and the interaction strength between the adsorbed water molecules and the pore surface [32].

Specifically, during mortar hydration where a pore network has been developed, the nuclear magnetization in a T_1 experiment, using a saturation recovery pulse sequence, cannot be described by a single exponential and is expressed as [32]:

$$R(t) = \frac{M_0 - M(t)}{M_0} = \int_0^\infty g(T_1)\exp(-t/T_1)dT_1 \tag{2}$$

where $R(t)$ is the proton magnetization recovery function, M_0 is the magnitude of the magnetization at equilibrium and $M(t)$ is the observed magnetization as a function of time t. Here, $g(T_1)$ is the spin–lattice relaxation time T_1 distribution function, which according to Eq. (1) is related to the pore-size distribution function [23]. On the basis of Eq. (2), $g(T_1)$ can be resolved by means of an inverse Laplace transform, [32] revealing important information about the porous microstructure in the hardened material.

2. Experimental

2.1. Sample preparation

Two different lime–pozzolan pastes were prepared to study the evolution of the pore structure during setting. The system consisted of hydrated lime powder ($Ca(OH)_2$), (Merck, Germany) and a natural pozzolan powder of volcanic origin. The natural pozzolan used was a commercial product available in Greece, namely Ifestiaki Gaia (IG), a finely ground product with particle size <20 μm supplied by Dalkafoukis, Greece. The mineral phases present in the hydrated lime powder are mainly portlandite and traces of calcite, whereas the mineral phases present in the pozzolan powder consisted of quartz, illite/muscovite, kaolinite and Na-feldspars (albite, anorthoclase). The iron content (Fe_2O_3) of the pozzolan was 2.6% (w/w).

The pastes were prepared by slightly modifying the EN 196-1 [33] standard for cement paste production. In particular, de-ionized water and lime were mixed thoroughly using a planetary mixer. Once water was added to the lime powder, the resultant paste was mixed for 90 s at 140 rpm and another 90 s at 285 rpm. Then, natural pozzolan was added to the hydrated paste and mixed for 90 s at 140 rpm. The mixing process was interrupted for 90 s and then mixed again for 90 s at 285 rpm. The lime to pozzolan ratios were 50:50 and 30:70 (w/w) in the mixtures CaIG5 and CaIG7, respectively. In both mixtures, the water added was 90% (w/w) of the solid constituents. After mixing, the samples were sealed into NMR glass tubes using Parafilm® membrane to avoid moisture loss and then, immediately placed into the spectrometer. The sample dimensions were 9 mm in diameter and 30 mm in height. The water content of each mixture satisfies the requirement for optimum flow characteristics [34], while the mixtures present a flow value of 180 mm.

A second batch of the above mixtures was moulded in prismatic moulds, with the dimensions 20 × 20 × 80 mm, and then placed in a curing chamber for setting at RH = 95 ± 3% and $T = 25 \pm 2$ °C. These specimens were used for monitoring the evolution of the microstructure and phase formation during setting by SEM and MIP.

2.2. NMR relaxometry

^{1}H NMR spin–lattice T_1 relaxation experiments were conducted using a home-built circular Halbach array magnet,