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Monitoring the hydration of MgO-based cement and its mixtures with Portland cement by ^{1}H NMR relaxometry

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ABSTRACT

The hydration process of MgO-based cement, Portland cement, and several mixtures of them was investigated for 1 month by measuring ^{1}H transverse relaxation times (T_2) of the different fractions of water inside pastes by means of the Carr-Purcell-Meiboom-Gill pulse sequence. The obtained T_2 distributions were exploited to get information on the kinetics of the hydration process and on the evolution of the porous structure of the calcium silicate hydrate (C-S-H) and magnesium silicate hydrate (M-S-H) binder phases as a function of time. The analysis of solid echo ^{1}H Free Induction Decays was employed to determine the relative amount of hydrogen-containing solid phases present in pastes at the longest hydration time.

1. Introduction

In recent years, MgO-based cements have been proposed both as potential low-CO_2 alternatives to Portland cement, the dominant form of cement used worldwide, and as low-pH cements for nuclear waste immobilization [1].

The binder phase of these cements is magnesium silicate hydrate (M-S-H), the amorphous phase that forms from the reaction of MgO with a source of silica and water. Although a significant quantity of literature exists concerning the structure and nature of the M–S–H gel [2–7], the understanding of M–S–H as a binder phase is in its infancy. In particular, questions are still open concerning the hydration of MgO/SiO_2 mixtures, even if this process is fundamental for the formation of the binder phase, ultimately determining microstructural properties such as composition, porosity, and water distribution, which in turn control the mechanical properties of cement. In recent papers, the inferior mechanical properties of MgO-based cements with respect to traditional CaO-based cements have been correlated to the different structures of the respective binder phases (i.e M-S-H and C-S-H (calcium silicate hydrate)) at the nano- and micro-metric scale [8], as well as to the different distribution of water inside them [9]. In particular, it has been shown that poly-disperse spherical globules (without an internal layered structure) packed into a fractal structure constitute M-S-H at variance with C-S-H, where, according to the Jennings model [10], colloidal disc-like globules, with a layered substructure including water, pack in flocs. Moreover, the higher compressive strength of C-S-H with respect to M-S-H has been associated to a higher amount of structural and constrained water, the latter being in turn considered as an indication of a smaller average pore size.

The hydration of cement is a very complex process in which reactants dissolve in water and hydrated phases precipitate to form gels with a porous structure that evolves in time. In the case of Portland cement, calcium silicates (alite and belite) and aluminates dissolve and C-S-H forms together with Portlandite and minor amounts of calcium-aluminate phases. In the case of MgO/SiO_2 mixtures, MgO dissolves giving rise to Mg^{2+} and OH^- ions; when a saturation concentration is reached, brucite precipitates and a moderately basic pH is established, which favors the hydration of silica with formation of silicate anions. From the reaction between

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silicate anions and Mg^{2+} cations M-S-H forms at the expense of brucite and silica [3].

^1H NMR relaxometry, through the non invasive measurement of transverse (T_2) and/or longitudinal (T_1) relaxation time(s) of protons directly on as prepared pastes, gives unique information on the kinetics of formation of hydrogen-containing solid phases and on the evolution of the state of water and the pore network during cement hydration [11–14]. In particular, analyses of ^1H Free Induction Decay (FID) on Portland cement pastes allowed protons in solid phases to be singled out and quantified [15–17]. Moreover, the dependence of the T_2 values of protons of water inside pores on the surface-to-volume ratio of pores and on a specific surface relaxivity has been exploited to distinguish and quantify different water populations [18–21]. Under the assumption of fast diffusion conditions and fully saturated pores [22,23], the distribution of pore sizes in the C-S-H gel and its evolution in the different stages of cement hydration have been determined [24,25].

In the present work, ^1H NMR relaxometry is employed for the first time to investigate the hydration process of MgO-based cements. To this aim, T_2 measurements were performed using the Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence [26] at different times, ranging from ~0.5 h to ~1 month, during the hydration of a 1:1 mol:mol mixture of highly reactive periclase and fumed silica, either alone (MS100) or mixed with different proportions of ordinary Portland cement (MS80C20, MS50C50, and MS20C80). The hydration of the sole Portland cement (C100), carried out under the same conditions, was also investigated for comparative purposes. Moreover, ^1H FID analyses on pastes of all samples hydrated for ~1 month were exploited to highlight the presence of hydrogen-containing solid phases. The results were discussed taking into account findings on the nature and structure of the hydrated phases obtained by other techniques [27,28].

2. Experimental

^1H NMR measurements were performed at 20.7 MHz and 24 °C using a Niumag permanent magnet interfaced with a Stelar PCNMR console. The temperature was controlled within ±0.1 °C with a Stelar VTC90 variable temperature controller. The 90° pulse duration was 3 μs. CPMG measurements [26] were carried out with an echo time (τ) of 20 μs and acquiring 120 scans. Solid echo experiments were performed with an echo delay of 14 μs and acquiring 120 scans. The recycle delay was 2 s.

For the NMR measurements, pastes prepared as described in the Supplementary material were deposited at the bottom of 5 mm NMR tubes and tightly sealed with Parafilm. Samples were stored at 24 ± 1 °C in a temperature-controlled room during hydration. Measurements were performed at different hydration times and the reproducibility of the results was tested by comparing measurements on at least two independently prepared samples.

Relaxation decay data from CPMG experiments were inverted to give T_2 distributions by the algorithm UPEN [29,30] implemented in UpenWin 1.05 software [31]. Experimental FIDs acquired on resonance using the solid echo pulse sequence were fitted to a linear combination of a Gaussian and one or two exponential functions using a non-linear least squares procedure implemented in the Mathematica [32] environment. Solid echo FIDs were used to determine the fraction of protons arising from reacted water in solid phases (given by the fractional weight of the Gaussian function) and the corresponding T_2 value. The longer exponential decay(s), ascribable to unreacted water with different degree of mobility, and more affected by magnetic field inhomogeneity, was (were) instead determined by the CPMG experiments.

3. Results

Representative examples of T_2 distributions obtained from CPMG data are shown in Fig. 1 for all samples; vertical expansions are reported in Fig. S1. When well-separated T_2 peaks are observed, trends of T_2 values at the maxima and corresponding proton populations are also reported as a function of the hydration time, t_H, in Fig. 2 and Fig. S2, respectively.

For C100, at $t_H < 6$ h two T_2 peaks centered at ~3 and 12 ms with relative weights of ~20 and 80% are observed (Fig. 1), both

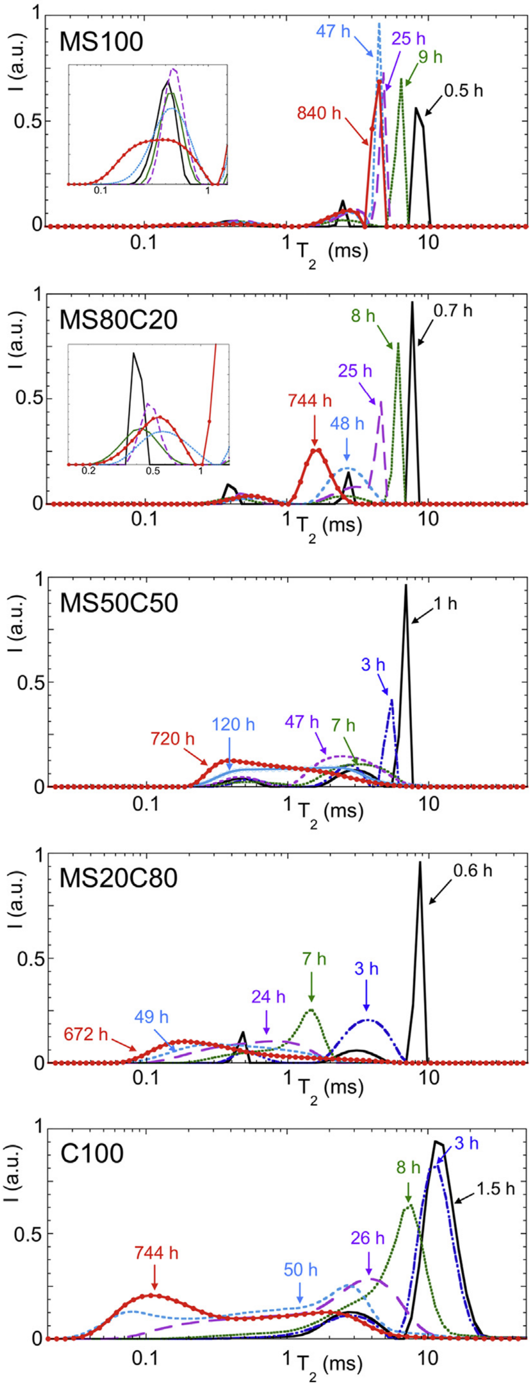

Fig. 1. Representative selection of ^1H T_2 relaxation time distributions from CPMG experiments at different hydration times. Vertical expansions of these distributions are reported in Fig. S1.

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