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The effect of curing relative humidity on the microstructure of self-compacting concrete

Sofía Aparicio [a,*], Sagrario Martínez-Ramírez [b], Miguel Molero-Armenta [a], José V. Fuente [c], Margarita G. Hernández [a]

[a] Instituto de Tecnologías Físicas y de la Información "Leonardo Torres Quevedo", ITEFI (CSIC), C/Serrano 144, 28006 Madrid, Spain
[b] Instituto de Estructura de la Materia (CSIC), C/Serrano 113 bis, 28006 Madrid, Spain
[c] Instituto Tecnológico de la Construcción, AIDICO, Parque Tecnológico, Avda. Benjamín Franklin 19, 46980 Paterna (Valencia), Spain

HIGHLIGHTS

- The samples cured at 70% RH present more tetrahedrally coordinated aluminium.
- More aluminium is taken up by the C—S—H gel in the samples cured at 70% RH.
- The transformation of ettringite to AFm is promoted at 70% RH.
- The samples cured at 98% RH present lower mean chain lengths of the C—S—H gel.

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ABSTRACT

A study was conducted to investigate the effect of the curing relative humidity on the microstructural properties of SCC with limestone filler. Two curing conditions were considered with humidities of 98% and 70%. Three microstructural techniques were employed to study the hydration: TGA, Micro-Raman spectroscopy and NMR. It was found that the samples cured at 70% humidity present more tetrahedrally coordinated aluminium since more aluminium is taken up by the C—S—H gel and the transformation of ettringite to AFm is promoted. The samples cured at 98% humidity are more hydrated but present lower mean chain lengths of the C—S—H gel.

1. Introduction

The use of self-compacting concrete (SCC) has increased significantly in the last years. The influence of different environmental conditions, specially the temperature, on the curing process of SCC has been studied by several authors [1–3]. The influence of curing temperature on mechanical properties of cementitious materials is widely known. High temperatures modify the behaviour of compressive strength increasing rapidly at early stages but reaching lower values at final stages than curing at 20 °C. Nevertheless, it is also important to analyse how the initial curing conditions affect the microstructural properties of SCC.

The effect of curing temperature on hydration products has been studied by several authors [4–8]. In these studies, it was found that high temperatures modified the structure of C—S—H gel, indicating that high temperatures produce C—S—H gel with Q^2 units. These microstructural studies were conducted on cement pastes or mortars, but not in concrete, therefore the effect of the limestone filler it was not observed. Although the curing process is influenced by the environmental temperature and humidity, the effect of humidity is a topic poorly studied from the microstructural viewpoint. The effect of reduced relative humidities in clinker mineral hydration was studied by [9]. While [10] discusses why alite stops hydrating below 80% relative humidity from a thermodynamical point of view.

Among the microstructural techniques commonly used to characterise the non-crystalline phases formed after hydration of cement-based materials are Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR) and Raman spectroscopy. Both techniques provide the information about the polymerisation of C—S—H gel and the remaining hydrated phases.

The influence of limestone filler on cement hydration composition has been widely analysed on the literature [11–20]. Early in

* Corresponding author.
E-mail addresses: sofia.aparicio@csic.es (S. Aparicio), sagrario@iem.cfmac.csic.es (S. Martínez-Ramírez), miguel.molero@gmail.com (M. Molero-Armenta), jofuera@gmail.com (J.V. Fuente), m.g.hernandez@csic.es (M.G. Hernández).

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the 1990s, several studies showed that limestone seems to favour crystallization of monocarbonate rather than monosulfate [11–13], with the consequence of increasing the amount of ettringite [11]. In [14] thermodynamic calculations as well as experimental observations indicated that in the presence of limestone, monocarbonate instead of monosulfate was stable. The authors in [15] studied the influence of limestone powder used as filler in SCC compared with traditional concrete and high performance concrete, and they confirmed that the limestone powder does not participate in chemical reaction by thermal analysis and BSE image analysis. Other publications were found in the bibliography reporting the active participation of limestone in the chemical reaction of cement [21,22].

In this paper, the effects of curing relative humidity on the microstructural properties of SCC adding limestone filler were studied using different techniques. Two different curing conditions were considered with a constant temperature of 20 °C and varying the relative humidity (RH), one with 98% and the other one with 70%. The microstructural behaviour after 7 and 28 days was studied by thermogravimetric analysis, ^{27}Al and ^{29}Si nuclear magnetic resonance and Micro-Raman spectroscopy.

2. Experimental description

The materials, curing conditions, and the experimental setup used in this work are described below

2.1. Materials and curing conditions

All specimens were made with white cement BL I 52.5 R. The chemical and mineralogical composition of the cement use is given in Table 1.

The mixtures of SCC were manufactured and cast at the AIDICO laboratory. The proportions of the SCC components are presented in Table 2. The mixture was prepared according to the standard specifications [24]. The mixtures were deposited in cylindrical moulds of 100 × 200 mm. The free surface of the moulds was sealed to prevent desiccation. Subsequently, these specimens were exposed to two different curing conditions (CCs) and they were demoulded after 24 h and kept in the same conditions during 28 days. In total four specimens were fabricated and cured under the different CCs.

Table 3 shows the particle size distribution values of the limestone filler, it was determined by laser diffraction at the AIDICO laboratory [25].

Two different CCs were considered in this experiment. CC1 refers to the curing process recommended by the standard specifications [24] and it was made in a moist room with constant conditions of 20 °C temperature and 98% of RH. CC2 was made in a moist room with controlled and constant temperature and moist of 20 °C and 70%, respectively.

2.2. Workability test of SCC

Deformability and viscosity of fresh SCC were evaluated through the measurement of slump flow diameter, the J-ring (Japanese ring) and the V-funnel flow time test according to standards [26–28]. This specification accepts a slump flow diameter ranging from 550 to 850 mm for SCC, an elapsed time less than 25 s for V-funnel flow time, and for the J-ring test a difference in height less than 10 mm between the concrete inside and outside the bars. The results of the workability tests are presented in Table 4. It can be seen that the values obtained using the different tests agree with the above specifications.

2.3. Microstructural studies

In this work microstructural properties were conducted to study the influence of the curing process of SCC on the final properties of these materials. The microstructural studies comprised thermogravimetric analysis, Micro-Raman spectroscopy and ^{27}Al and ^{29}Si MAS NMR. These studies were performed after 7 and 28 days of curing in small pieces (about 2 × 3 × 2 cm) of the concrete obtained from the compressive strength test. The small pieces were extracted from the core of the specimens by cracking. The hydration reaction was stopped by immersing the samples in acetone during 72 h. Before the microstructural testing the small pieces were desiccated by vacuum drying at ambient temperature during 6 h.

Table 2
Mixture proportions of SCC with an estimated error of 0.1 g.

White limestone sand 0/4 (kg/m^3)	876.1
Limestone gravel 6/12 (kg/m^3)	895.0
Cement BL I 52.5 R (kg/m^3)	231.7
Limestone filler Omyacarb 10BE (kg/m^3)	154.5
Superplasticizer viscocrete 5920 (kg/m^3)	3.2
(Water/binder)$_{total}$ ratio	0.53

Table 3
Particle size distribution values of micron size materials [25].

	<3 μm, %	3–32 μm, %	>32 μm, %
$CaCO_3$ Omyacarb 10BE	5.14	65.41	29.45

Table 4
Workability tests of the SCC.

Slump flow (mm)	653
V-funnel (s)	16
J-ring (mm)	6
Fresh density (kg/m^3)	2259

2.3.1. Thermogravimetric analysis (TGA)

The thermogravimetric study was used for the determination and quantification of total chemically bound water, calcium hydroxide and water in the hydration products in dried concrete samples using the Mettler Toledo TGA/SDTA851 equipment which does not require using a reference material. This equipment allows to determine TG and DTA curve simultaneously. The samples were ground considering a maximum particle size of 0.2 mm and they were heated from 25 to 1000 °C at a constant rate of 10 °C/min in an inert N_2 atmosphere (75 ml/min).

2.3.2. Micro-Raman spectroscopy

Raman spectra were recorded with a confocal Raman microscope (Renishaw RM2000) equipped with a 633-nm laser, a Leica microscope, and a thermoelectrically cooled CCD camera. The spectra shown were obtained with a 50× objective lens. The laser output was 100 mW, and the exposure time 10 s. Two software applications, Galactic Industries GRAMS/32TM and Origin 8.0, were used for data collection and analysis. Ten scans were recorded to improve the signal-to-noise ratio. The area where vibration modes are found, i.e. 4000–100 cm^{-1}, was the spectral region scanned. Calibration was done using the 520.5 cm^{-1} line of a silicon wafer.

2.3.3. ^{27}Al and ^{29}Si MAS NMR

A Bruker MSL-400, Billenca, MA spectrometer was used to obtain the solid sample ^{29}Si and ^{27}Al NMR spectra. The ^{29}Si MAS NMR experiments employed ν_R = 5 kHz, a pulse width of 3 μs corresponding to a π3 rad. pulse length, ^1H decoupling of $\gamma B_2/2\pi$ = 50 kHz, a relaxation delay of 20 s, and typically 3000 scans. The ^{29}Si chemical shifts were recorded against Tetramethyl-silane (TMS) and the ^{27}Al shifts against an aluminium trichloride solution. The spectra were analysed and fitted using peak shapes with the dmfit spectral analysis software [29].

3. Results and discussion

The results and conclusions obtained with the different microstructural techniques are presented below:

Table 1
Cement chemical and mineralogical composition (% by weight) [23].

SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	SO_3	K_2O	TiO_2	P_2O_5	P.F.	CaO_{free}
21.71	4.85	0.32	0.88	65.08	0.15	3.82	0.57	0.12	0.06	2.39	0.65

C_3S = 64.12%, C_2S = 13.21%, C_3A = 12.16%, C_4AF = 0.97%.