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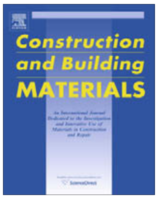

The effect of curing temperature on white cement hydration

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A R T I C L E I N F O

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Cement manufacture has undergone extensive change in its attempts to rise to the successive challenges posed by society. The hydration of Portland cement is a complex phenomenon that depends on both reagent characteristics and reaction conditions. It is a well-known fact that the curing temperature plays an important role on the hydration kinetics. The present study is the first to be undertaken on the effect of curing temperature on white Portland cement paste hydration over long hydration times (365 days at 20 °C and 124 days at 60 °C). The technique used, ^{29}Si and ^{27}Al NMR spectroscopy, is particularly well adapted to the study of cement hydration. White cement hydration generates a C–S–H gel in which the aluminium taken up forms bridge bonds. After nine days at 60 °C, the degree of reaction expressed in terms of the Al(IV)/Al(VI) ratio nearly doubles the value found after 90 days at 20 °C.

1. Introduction

In the last century or so, in light of the advantages it features over other materials such as stone, wood or steel, Portland cement has become the most widely used artificial construction material. Cement manufacture has undergone extensive change in its attempts to rise to the successive challenges posed by society. The hydration of Portland cement and its components is a complex phenomenon that depends on both reagent characteristics (chemical composition, crystalline structure, fineness and so on) and reaction conditions (*w*/*c* ratio, chemical species and so on) [1–3]. Curing temperature is widely known to play an important role in hydration kinetics, based on any number of studies. Frías [4–6] have reported the significant changes on reaction kinetics, microporosity and hydration degree in MK-blended cement pastes when the curing temperature increased from 20 °C to 60 °C. Other researchers [7–10] found the hydration rate to increase with temperature in Portland cement, particularly at lower degrees of hydration, with the effect tapering as hydration progressed. Of all the individual clinker minerals, only C_2S shows any significant acceleration, which continues several months after mixing with water [8]. In this same vein, Xiadong and Kirpatrick [11] described structural and compositional diversity to be one of the major characteristics of C–S–H, citing structural variation under different curing conditions as a foremost example. In synthetic C–S–H with a C/S ratio of from 1.13 to 1.56, cured at relative humidities ranging from 9% to 100% and temperatures from 25 to 200 °C, the samples forming in the upper temperature range, with all other conditions unvaried, were found to be more highly polymerized and to have both a less orderly structure and smaller basal spacing than the gels forming at room temperature.

Another major area of research has focused on aluminate phase stability with rising curing temperature. Of the results obtained, perhaps the most prominent were reported by Older et al. [7], who found that ettringite was rapidly replaced by monosulphate at 75 °C and that monosulphate itself disappeared after curing at temperatures of around 100 °C.

As Scrivener and Wieker [12] noted, however, despite the research conducted on the effect of temperature on Portland cement reaction mechanisms and microstructure, the impact of this parameter on hydration remains unclear. The explanation may well lie in the lack of rigorous comparative data on hydration in: cements of the same composition under different conditions; cements of the same composition but different particle size distributions; cements with different compositions, and so on. In a study aimed at exploring these very concerns, Paul and Glasser [13] reported substantial changes in Portland cement paste mineralogy and microstructure when cured for 8.4 years under different temperatures (20 and 85 °C). At 20 °C, the matrix consisted in relatively coarse, blocky $Ca(OH)_2$ crystals along with a certain amount of Aft (ettringite) embedded in a groundmass of C–S–H. At 85 °C, by contrast, the mineralogy consisted in four solid hydrates: $Ca(OH)_2$, C–S–H gel, katoite and a hydrotalcite-like phase, in the presence of 30% anhydrous clinker. Hirljac et al. [14] reported that curing temperature affected silicate polymerization and the distribution of polymerized substances during alite hydration.

To date, most of the literature has focused primarily on the effect of temperature on the reaction kinetics of grey Portland cement and derivatives, while there is a dearth of experimental data on other materials, such as white Portland cement. In a previous paper, Martínez-Ramírez et al. [15] described a comprehensive

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micro-Raman study on white cement hydration cured at 20 °C for 360 days.

The present study is the first to be undertaken on the effect of curing temperature on white Portland cement paste hydration over long hydration times (124 days at 60 °C). The results were compared to the findings for the same white cement cured at 20 °C for 365 days. The technique used, ^{29}Si and ^{27}Al NMR spectroscopy, is particularly well adapted to the study of cement hydration.

2. Experimental procedure

2.1. Materials

The chemical and mineralogical composition of the white cement used is show in Table 1. All cement pastes were prepared with a water/cement ratio of 0.55 by weight and placed in plastic airtight containers at 100% RH. Half of the specimens were cured at room temperature and the other half were cured in a laboratory oven at 60 °C. After each predetermined curing time (3d, 90d and 360 days for samples cured at 20 °C and, 30 h, 9d and 124 days for samples cured at 60 °C). The hydration reaction was stopped using a laboratory oven at 105 °C during 24 h.

2.2. Instrumental technique

A Bruker MSL-400, Billenca, MA spectrometer, working at resonance frequencies of 79.49 and 104.26 MHz was used to obtain the solid sample ^{29}Si and ^{27}Al NMR spectra, which were recorded following (4 μs) π/2 excitation pulses with 5 s relaxation delays. The scan numbers were 800 for ^{29}Si and 200 for ^{27}Al. Sample spin rates were 4 and 12 kHz, respectively. The ^{29}Si chemical shifts were recorded against tetramethylsilane (TMS) and the ^{27}Al shifts against a 1 M solution of $AlCl_3 \cdot 6H_2O$. The spectra were analyzed with Origin (version 6.0) computer software.

3. Results and discussion

3.1. ^{27}Al and ^{29}Si NMR at 20 °C

Fig. 1 shows the ^{27}Al NMR spectra for an anhydrous white cement and for the same cement after hydration at 20 °C for different lengths of time. The spectra contained signals for tetrahedrally and octahedrally coordinated aluminium. Initially, only tetrahedral aluminium signals appeared at 80 ppm, with a shoulder at 66 ppm. After cement hydration, new signals appeared in tetrahedral and octahedral Aluminium areas.

Table 1
Chemical composition of white cement

Oxides	Percentage (wt)
SiO_2	23.65
Fe_2O_3	0.22
Al_2O_3	3.34
CaO	67.09
MgO	0.79
K_2O	0.84
Na_2O	0.9
SO_3	1.82
L.O.I[a]	1.12
Specific surface	1.04 m^2/g
	C_2S = 14.70%
	C_3S = 70.54%
	C_3A = 8.48%
	C_4AF = 0.67%

[a] Loss on ignition at 1000 °C.

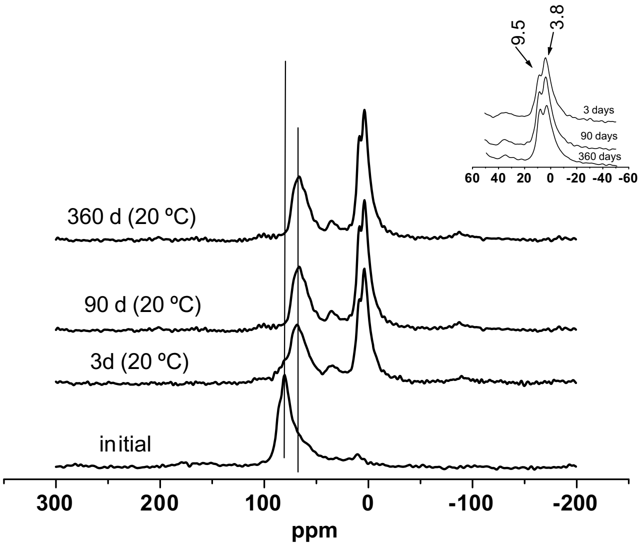

Fig. 1. ^{27}Al NMR spectra for anhydrous and 3-, 90- and 360-day hydrated white cement (T = 20 °C).

The two new peaks in the octahedral Al area, at 3.8 and 9.5 ppm, denote the formation of new phases. Andersen et al. [16] found that the signal at 9.8 ppm was due to the appearance of a monosulphoaluminate, and reported an ettringite signal at 13.1 ppm. Ettringite was not observed in our samples since they were dried at 105 °C, which is a higher temperature to ettringite decomposition (below 60 °C). A signal detected at 9.5 ppm in the present samples was attributed to the presence of monosulphoaluminate.

Identification of the signal at 3.5 ppm entails some difficulty. Sun et al. [17], studying synthetic C–S–H gel with substitution Al, observed that when the Al/(Si + Al) ratio was 0.29 a signal appeared at 4 ppm, which they attributed to the presence of C_3AH_6 and strätlingite. If it the product found here were strätlingite, Q^4 signals (at around 90 ppm) should have appeared in the ^{29}Si NMR spectrum [18] and no signals were found at 90 ppm. All these results agree with Frías and Cabrera [19] whose failed to detect the formation of these phases in XRD or DTA analysis of unadditioned white cement. However, Schneider et al. [20] attributed this same peak to the presence of C_3AH_6 in cement pastes containing activated slag. Martínez-Ramírez et al. [15], analyzing white cement hydration with Raman spectroscopy, observed the formation of sulphate-containing phases that they were unable to identify. Klimesch and Ray [21] observed a resonance for octahedrally coordinated Al at approximately 3–5 ppm, which they ascribed to Al substitution in an octahedral site on the torbermorite structure. Andersen et al. [16] reported a low frequency resonance (4.0 ppm) during white cement hydration which they regarded to be due to the formation of a less-crystalline alumina gel or a calcium aluminate hydrate, Skibsted et al. [22], in turn, reported no signal at 3–4 ppm in their ^{27}Al NMR spectroscopic characterization of the anhydrous and hydrated phases of calcium aluminate in cements. Clearly, then, further research is required to identify this phase.

The ratio between the intensities of the signals due to octahedral Al changed with hydration time. Initially, the peak at 3.8 ppm was larger than the one at 9.5 ppm. The 90-day spectra showed that both signals grew, while the intensity of the peak at 3.8 ppm declined after 360 days of hydration. All these findings denote the instability of the compound formed and its decomposition or reaction with others at longer hydration times.

Changes were observed in the tetrahedral Al signals (80 and 66 ppm) from the third day, with the peak at 80 ppm waning and the one at 66 ppm intensifying substantially. The initial