

THE EFFECT OF CURING TEMPERATURE ON WHITE CEMENT HYDRATION

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Abstract

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.

Keywords: White cement, Reaction Kinetics, NMR, Curing temperature

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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) [1-5]. Curing temperature is widely known to play an important role in hydration kinetics, based on any number of studies. Frías et al. [6-8] 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 [9-12] 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 C₂S shows any significant acceleration, which continues several months after mixing with water [10]. In this same vein, Xiadong et al. [13] 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.

[9], 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 et al. [14] 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 et al. [15] 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. Hirljact et al. [16] 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. [17] described a comprehensive 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 shown 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 hours.

2.2 Instrumental Technique

A Bruker MSL-400, Billerica, 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) $\pi/2$ excitation pulses with 5-second 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 1M solution of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$. 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

Figure 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.

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. [18] 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. [19], 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 C₃AH₆ and strätlingite. If it the product found here were strätlingite, Q⁴ signals (at around 90 ppm) should have appeared in the ²⁹Si NMR spectrum [20] and no signals were found at 90 ppm. All these results agree with Frías et al. [21] whose failed to detect the formation of these phases in XRD or DTA analysis of unadditioned white cement. However, Schneider et al. [22] attributed this same peak to the presence of C₃AH₆ in cement pastes containing activated slag. Martínez-Ramírez et al. [17], analyzing white cement hydration with Raman spectroscopy, observed the formation of sulphate-containing phases that they were unable to identify. Klimesch and Ray [23] 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. [18] 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. [24], in turn, reported no signal at 3-4 ppm in their ²⁷Al

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 tetrahedral Al signal at 80 ppm was ascribed to the Al in alite and belite. The signal appearing after sample hydration (66 ppm) was attributed to the Al taken up by the C-S-H gel [25].

In Figure 2, which shows the variation in ^{29}Si detected by NMR, a resonance can be seen in the initial sample at -71.7 ppm (silicon in belite) along with a wide signal between -68 and -76 ppm attributed to a monoclinic form of alite, M_{II} [18].

After three days of hydration, the Si was observed at -79.6 (Q^1) ppm, while after 90 days the silicon at -71.7 ppm declined and a new signal appeared at -85.1 ppm. After 360 days of hydration, the Si attributed to the anhydrous phases had nearly disappeared and the peak at -85.1 (Q^2) ppm, assigned to the hydrated phases, had increased. No signal was observed at -90 ppm, confirming the absence of strätlingite.

Table II lists the signals and associated areas for the anhydrous and hydrated (at 20 and 60 °C) white cement samples.

The signals due to the Q^1 units (between -77 and -80 ppm) declined with reaction time, indicating that the monomers combined to form longer chains. The appearance of signals

attributed to Q^2 units containing no or only one atom of substitution aluminium and their growth with hydration time denoted Al addition into the C-S-H gel.

The mean chain length ($MCL=2[Q^1 + Q^2(0Al) + 3/2(Q^2(1Al))]/Q^1$) [24] increased from 3.7 after three days of hydration to 4.9 after 360. The latter is similar to 4.8 reported in the literature [27] by studying synthetic C-S-H gels. In that study, the gels were obtained by activating synthetic slag with a 5M solution of KOH at 60 °C for one week. Andersen et al. [18] obtained lengths of 3.49 in white cement hydrated at 20 °C for one year, although they observed chain length to rise to values of 4.07 when the hydration solution used was $NaAlO_2$. It seems that Al taken up into C-S-H gel increases main chain length.

3.2 ^{27}Al and ^{29}Si NMR white cement at 60°C

Figure 3 shows single-pulse ^{27}Al NMR spectra for white cement hydrated at 60 °C for 30 hours and 9 and 124 days. The signals observed were the same as for white cement hydrated at 20 °C, the primary difference lying in the intensity of the octahedral aluminium signals (3.8 and 9.5 ppm). The signal at 9.5 ppm was observed to be more and the one at 3.8 ppm less intense after 124 days of hydration at 60 °C. The tetrahedral aluminium signal underwent only slight changes throughout the test; in other words, the amount of Al uptake in the C-S-H gel did not appear to be affected by hydration temperature.

Figure 4 shows the variation over time in the ^{29}Si NMR signals for white cement hydrated at 60 °C: note the disappearance of certain signals and the appearance of others. The Q^0 and Q^1 signals decreased while the Q^2 signals with no aluminium or one or two atoms of substitution aluminium increased.

The value of the mean chain length increases from 3.2 after 30 hours to 5.3 after 9 days of hydration at 60 °C. This chain length was similar to the figure found for cement hydrated at 20 °C for 3 days and 360 days respectively. After 124 days of hydration at 60°C the mean chain

length increases until 8.3. Increases temperature produce longer mean chain value as well as higher $Q^2(1Al)$ (Table II).

A plot of the $Al(IV)/(Al(IV)+Al(VI))$ and $Al(VI)/(Al(IV)+Al(VI))$ values at different ages (Figure 5) and the two temperatures (20 and 60 °C) showed that the amount of new hydrated Al phases ($Al(VI)$) increased with time, while the amount of Al taken up in the C-S-H gel ($Al(IV)$) declined. This would explain the increased intensity of the signals at -85 ppm attributed to $Q^2(0Al)$ units.

At 20 °C, more Al was taken up in the early ages by the C-S-H gel than for the formation of hydrated phases, although the reverse was observed at 60 °C, where the amount of Al forming hydrated phases grew; this would explain the enlargement of the peak at 9.5 ppm, attributed to monosulphoaluminate. At higher temperatures, moreover, the Q^2/Q^1 ratio rose. The findings reported by Masse et al. [28] and the data given in Table II confirm that C-S-H chain length as well as the amount of substitute Al increase with temperature. These data are consistent with the observations reported by Xiadong [13] to the effect that temperature enhances C-S-H gel polymerization.

The $Al[IV]/Al[VI]$ ratio, sustained by some authors [20, 29] to be a measure of the degree of reaction, is shown in Figure 6 for the two temperatures and various ages. From the outset, higher figures were observed at 60 than at 20 °C. Indeed, the degree of reaction after nine days at 60 °C was nearly double the value found after 90 days at 20 °C.

4- Conclusions

^{29}Si and ^{27}Al spectroscopy is a useful tool for studying hydration in white cement at different temperatures. The visible differences observed in the spectra in the present study led to the following conclusions:

- a) The same hydrated phases – monosulphoaluminate and C-S-H gel – are formed during white cement hydration regardless of whether the hydration temperature is 20 or 60 °C. The hydration rate increases with temperature, however.
- b) White cement hydration generates a C-S-H gel in which the aluminium taken up forms bridge bonds. This aluminium content grows with hydration time at 20 °C and 60 °C.
- c) Hydrated white cement contains an aluminium phase of undetermined composition that resonates in the ^{27}Al NMR spectrum at 3.8 ppm. This phase appears and is unstable at both temperatures.
- d) More monosulphoaluminate is formed at 60 than at 20 °C.
- e) C-S-H gel chain length increases with hydration time and with temperature.
- f) 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.

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Figure Captions

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

Figure 2.- ^{29}Si NMR spectra for anhydrous and 3-, 90- and 360-day hydrated white cement
(T= 20 °C).

Figure 3.- Single-pulse ^{27}Al NMR spectra for anhydrous and 30-hour and 9- and 124-day
hydrated white cement (T=60°C).

Figure 4.- ^{29}Si NMR spectra for anhydrous and 30-hour and 9- and 124-day hydrated white
cement (T=60 °C).

Figure 5.- Al(IV or VI)/Al(IV)+Al(VI) ratio versus hydration time. Hydrated white Portland
cement at 20 (top) and 60 °C (bottom).

Figure 6.- Al[IV]/Al[VI] ratio versus hydration time for white Portland cement at 20 and 60
°C.

Table I.- Chemical composition of white cement

Oxides	Percentage (wt)
SiO ₂	23.65
Fe ₂ O ₃	0.22
Al ₂ O ₃	3.34
CaO	67.09
MgO	0.79
K ₂ O	0.84
Na ₂ O	0.9
SO ₃	1.82
L.O.I [§]	1.12
Specific surface	1.04 m ² /g
	C ₂ S = 14.70%
	C ₃ S = 70.54%
	C ₃ A = 8.48%
	C ₄ AF = 0.67%

[§]Loss on ignition at 1000°C;

Table II.- ^{29}Si NMR chemical shifts in samples of different ages hydrated at two temperatures.
Associated areas in parentheses

20°C			60°C			Description
3 days	90 days	360 days	30 hours	9 days	124 days	
-71.6 (26.3)	-71.6 (17.2)	-71.7 (6.7)	-71.6 (24.8)	-71.7 (11.5)	-71.8 (4.7)	Q ⁰
-73.1 (19.1)	-73.6 (6.0)		-73.1 (15.5)	-73.3 (3.3)	-73.5 (2.3)	Q ⁰
-75 (2.1)	-75.9 (5.7)	-75.1 (8.0)	-75.1 (4.7)	-75.6 (7.6)	-75.1 (1.9)	Q ⁰
-77.6 (17.8)	-77.8 (10.9)	-77.6 (7.6)	-78.5 (13.8)	-78.1 (10.2)	-77.8 (10.5)	Q ¹ end unit
-80 (13.5)	-79.6 (19.1)	-79.2 (15.9)		-79.7 (11.2)	-79.2 (4.9)	Q ¹ end unit
	-81.3 (4.0)	-80.7 (13.7)	-81.4 (20.4)	-81.3 (14.3)	-80.3 (12.45)	Q ¹ (0Al)
-82.4 (10.9)	-82.2 (16.4)	-82.3 (12.7)		-83 (8.4)	-82.1 (14.1)	Q ² (1Al)
-85.2 (10.) ³	-84.5 (11.9)	-85.2 (21.4)	-84.8 (16.0)	-85.7 (27.5)	-85.9 (36.1)	Q ² (0Al)
	-86 (8.8)	-86.5 (14.1)	-86.5 (4.8)	-87.4 (6.2)	-86.5 (13.0)	Q ² (0Al)
MCL						
3.7	4.6	4.9	3.2	5.3	8.3	

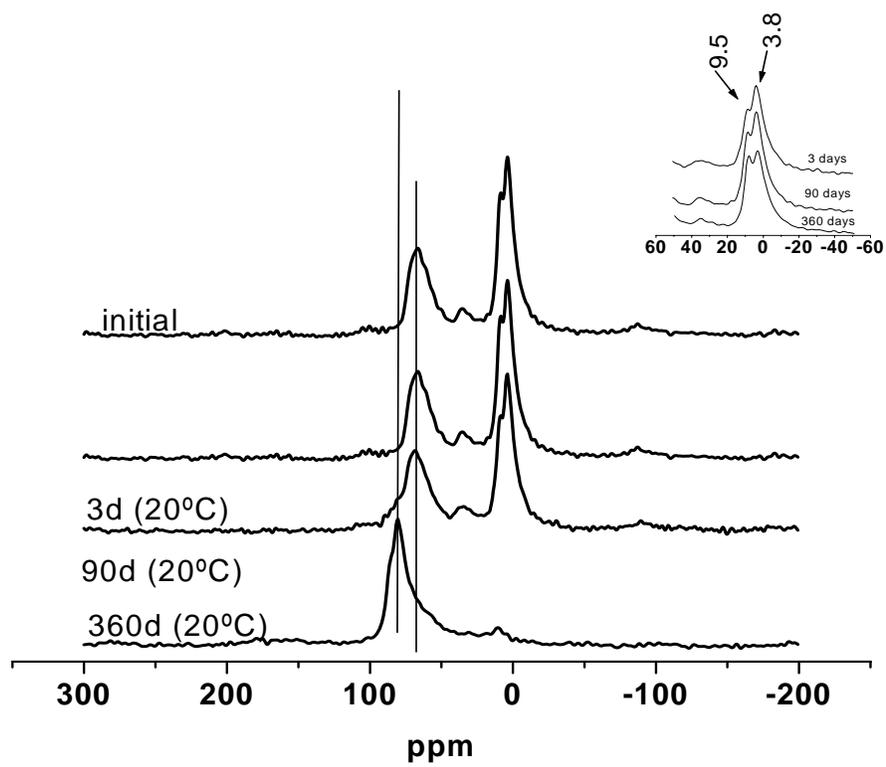


Figure 1

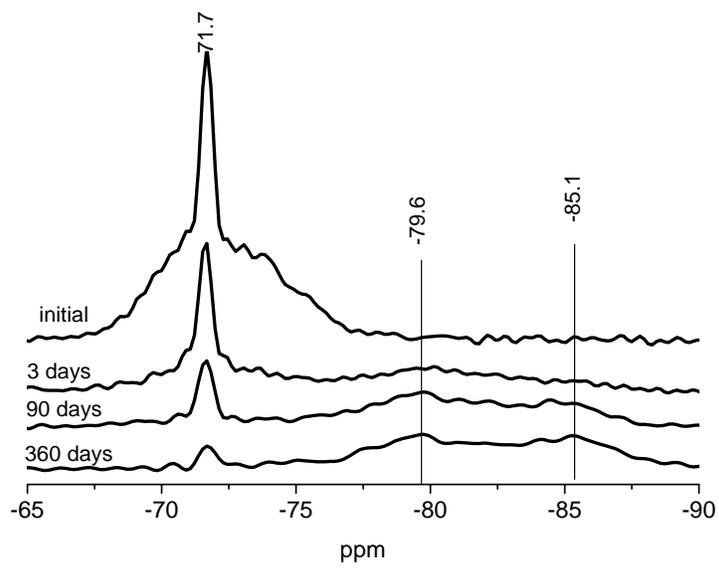


Figure 2

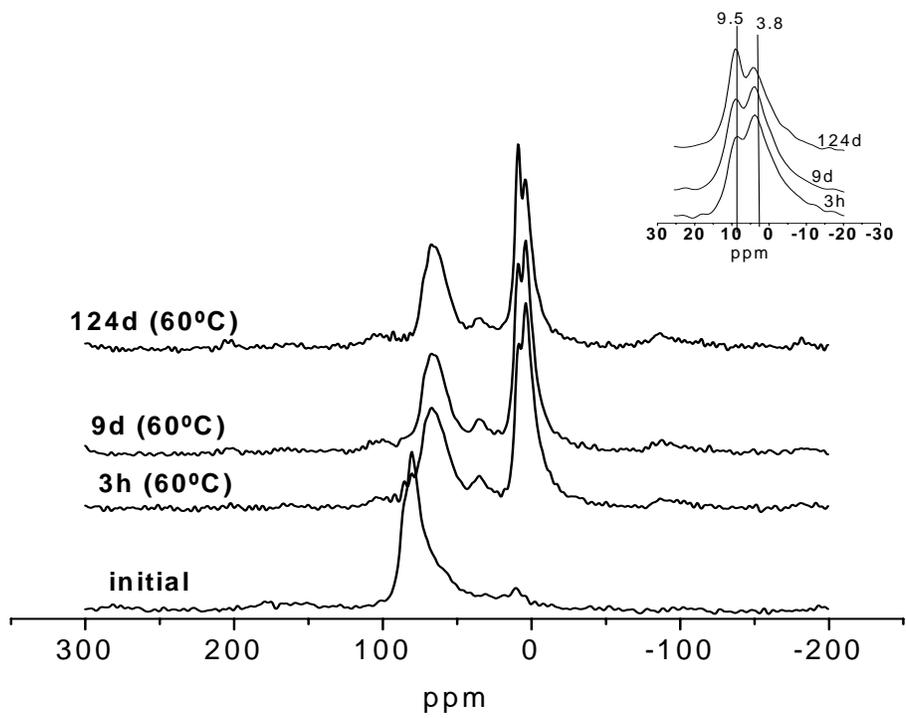


Figure 3

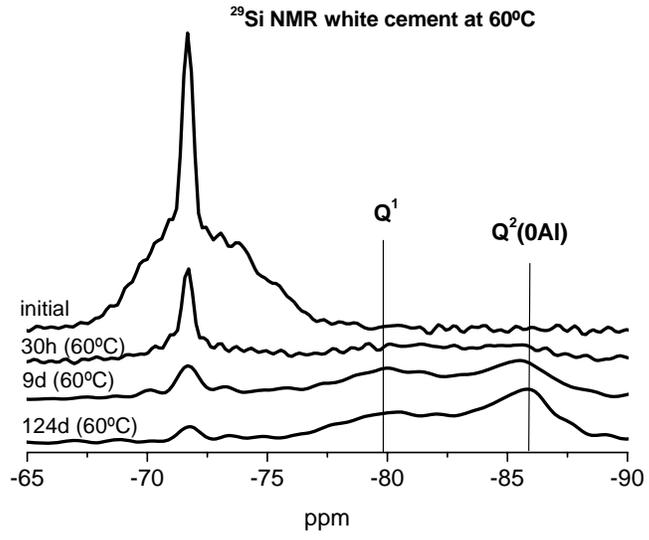


Figure 4

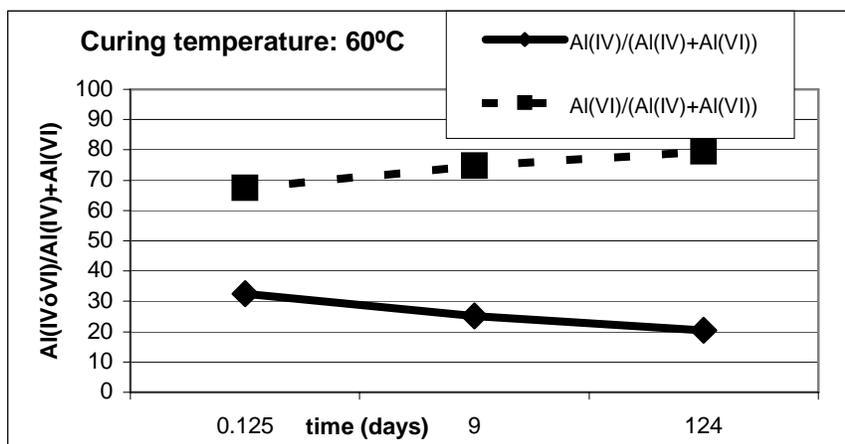
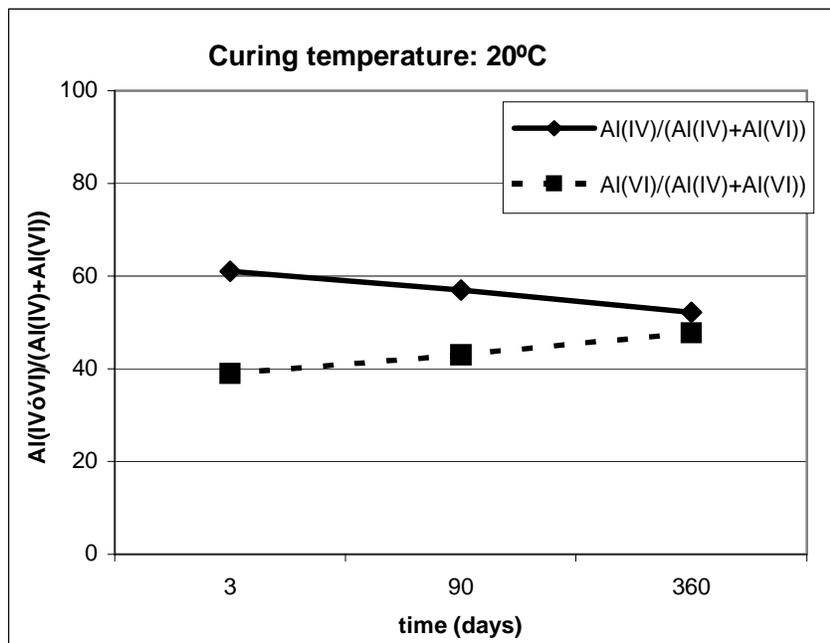


Figure 5

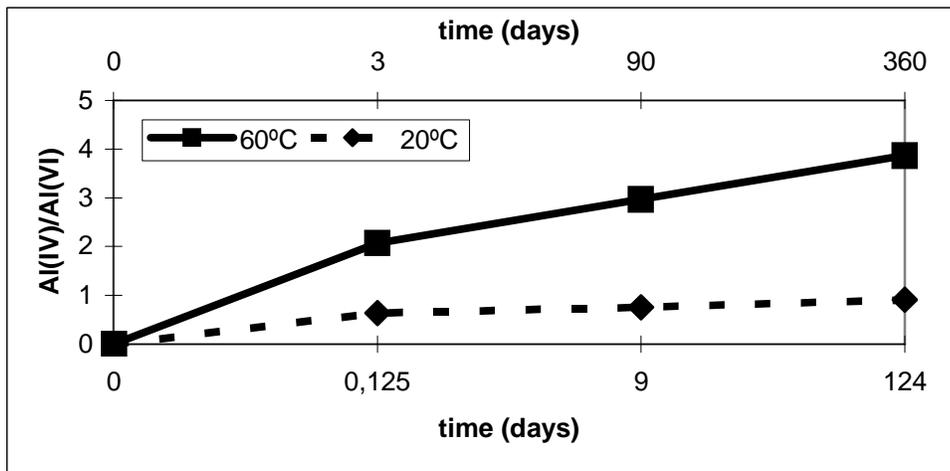


Figure 6