



## Characterization of aerial lime-based mortars modified by the addition of two different water-retaining agents

A. Izaguirre<sup>a</sup>, J. Lanás<sup>b</sup>, J.I. Álvarez<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry and Soil Sciences, School of Sciences, University of Navarra, c/Irunlarrea, 1, 31008 Pamplona, Spain

<sup>b</sup> CTH Navarra, Polígono Talluntxe II C/M, 10, 31192 Tajonar, Spain

### ARTICLE INFO

#### Article history:

Received 24 June 2009

Received in revised form 7 September 2010

Accepted 9 September 2010

Available online 17 September 2010

#### Keywords:

Admixture

Rheology

Freezing and thawing

Mechanical properties

Lime mortar

### ABSTRACT

Two different commercial additives that have been reported to act as viscosity enhancing, water retaining admixtures, namely hydroxypropyl methylcellulose and a guar gum derivative, were added to lime-based mortars in order to test their performance. Different properties of lime-based mortars were evaluated: fresh mixture behaviour through water retention, air content and setting time; hardened mixtures properties such as density, shrinkage, water absorption through capillarity, water vapour permeability, long-term compressive strengths, pore structure through mercury intrusion porosimetry and durability assessed by means of freezing–thawing cycles. Hydroxypropyl methylcellulose, unlike its well-known effect in cement-based materials, showed a very limited viscosity enhancing behaviour in aerial lime mortars. An adsorption mechanism of this additive on the  $\text{Ca}(\text{OH})_2$  crystals was reported to reduce its entanglement between chains and hence the viscosity of the pastes as well as its water retention ability. The guar gum derivative, which has a larger quantity of ionized groups at alkaline pH, reduced its adsorption onto slaked lime particles and gave rise to a clear increase in viscosity. However, this involved a larger water-retention capacity, which in fact resulted in a delay in setting time. The guar gum derivative proved to raise the air content, and changed the pore size distribution of the hardened mortars, thus improving the water absorption through capillarity and durability in the face of freezing–thawing cycles.

© 2010 Elsevier Ltd. All rights reserved.

### 1. Introduction

Viscosity-enhancing admixtures that also act as water retainers are very common in the field of cement mortars, modified cellulose ethers being the most widespread products [1–7]. Cellulose is a polysaccharide in a linear homopolymer form, which is insoluble in water due to strong molecular interactions via hydrogen. To make it soluble, some modifications must be performed. Etherification reactions constitute the main method, leading to products such as hydroxypropyl methylcellulose (HPMC) and hydroxyethyl methylcellulose (HEMC), which are the most widely used [1]. These products are expected to act as viscosity-enhancing admixtures, which improve the homogeneity of the mixture and enhance the workability of the mortar and some of the properties in the hardened mixtures [1,8]. In addition, another action of water-retaining agents consists of keeping the water in the mass over a longer period of time, which is supposed to improve cement hydration and, therefore, its mechanical strengths. A secondary effect of this role is a delay in the setting time of the mortar [1,2,5].

Although many studies focusing on cement mortars have been devoted to studying water-retaining agents derived from cellulose, how these products behave in lime-based mortars is not entirely understood. Seabra et al. [7] studied the influence of three different admixtures on the rheological behaviour of lime mortars. They stated that water-retaining agents are normally utilized to increase the mortar's viscosity, reducing the risk of material segregation during transport and handling, leading to a hardened product that has a better homogeneity and performance. They concluded that HPMC initially exerts a thickening effect on the mixtures but, after some shaking time, this tendency is reversed, due to excessive entrance of air. However, the influence of water-retaining agents on other important properties of the material – such as hardened state properties – has not been reported.

At this point, it is useful to highlight the growing scientific interest in lime-based mortars as well as their uses. Restoration work carried out on Cultural Heritage buildings requires the use of materials similar to those originally used, lime-based mortars being the most suitable choice for this purpose [9]. However, even though lime-based mortars have several advantages and are more compatible than cement mortars for use in repair work [10], some drawbacks still remain, such as: (i) long setting and hardening time; (ii) relatively low mechanical strength; (iii) high water absorption capacity through capillarity; (iv) major volumetric

\* Corresponding author. Address: Dpto. de Química, Fac. de Ciencias, Universidad de Navarra, C/ Irunlarrea, 1, 31.080 Pamplona (Navarra), Spain. Tel.: +34 948 425600; fax: +34 948 425649.

E-mail address: [jalvarez@unav.es](mailto:jalvarez@unav.es) (J.I. Álvarez).

change as a result of shrinkage [7]. As a general consideration, in order to reduce or even solve some of these problems, the potential use of admixtures might be considered. Previous work by the research group has shown some advantages related to the addition to aerial lime-based mortars of water repellents and a biodegradable polymer (starch), respectively [11,12]. Rodríguez-Navarro et al. [13], making a comparison between traditional aged slaked lime putty and dry hydrated lime reported that the use of dry hydrated lime, a very common industrial product, limits the capacity of  $\text{Ca}(\text{OH})_2$  particles to adsorb water and decreases viscosity and plasticity, thus being highly detrimental when a plastic binder is desired for mason/conservation purposes. As a result, research on some viscosity-enhancing agents for lime mortars made of dry hydrated lime is of particular scientific interest.

It should be noticed that since aerial lime mortars harden through two mechanisms: (i) loss of excess of water and subsequent compaction of the material and (ii) the carbonation process, the addition of water-retaining agents to non-hydraulic binders could also be damaging for these mortars to a certain extent, because if either the amount of mixing water is larger or the mixing water is retained over time, the excess of water could prevent  $\text{CO}_2$  from gaining access to the mortar, thus slowing down the carbonation process [12,14].

The present study was designed to fill the gap in the scientific literature concerning the performance of some thickening, water-retaining agents in aerial lime mortars. The rationale of the present study is that the viscosity-enhancing effect of the water retainers could be useful for aerial lime mortars enhancing their workability and giving non-sag and anti-slip properties to the mixtures. These aspects could improve the pump ability in spray-on mortars and would also be desirable for lime-based renders [12,15]. An assessment of the carbonation degree and the performance of modified lime-based mortars will be necessary to weigh up the above-mentioned advantages and the possible drawbacks related to the carbonation hindrance.

In the present study, two different commercial additives (water retaining and viscosity-enhancing agents) were tested in lime mortars in the fresh mixtures as well as in the hardened one, to assess the changes they produced in the samples. The selected admixtures were HPMC and guar gum derivative (hydroxypropyl guaran). A comparison between the performance of the two tested admixtures was also carried out.

## 2. Materials

An aerial commercial lime and a pure limestone aggregate were used to prepare the mortars. The lime (class CL 90-S according to Spanish standard [16]) was supplied by Calinsa (Navarra).

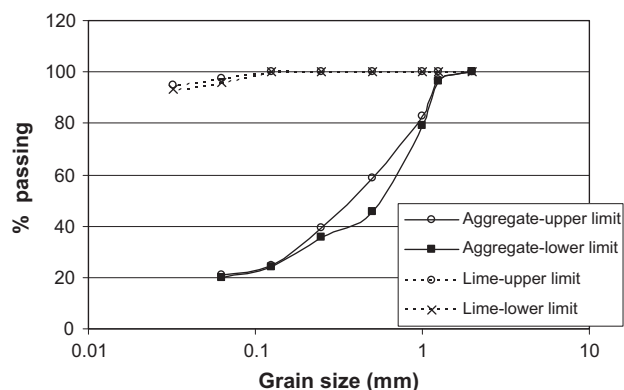


Fig. 1. Grain size distribution of lime and aggregate.

**Table 1**  
Mix proportions.

Samples	Composition (g)				
	Lime	Aggregate	HPMC	GG	Water
REF	341.7	1286.9	–	–	410
HPMC	341.7	1286.9	0.98	–	500
GG	341.7	1286.9	–	0.98	450

The mineralogical composition of this lime obtained by means of X-ray diffraction studies showed portlandite ( $\text{Ca}(\text{OH})_2$ ) as the main phase present in the sample. The aggregate was supplied by Caleras de Liskar (grupo HORPASA). This aggregate was a calcareous type, showing calcite as the main phase and a small amount of quartz, as the XRD analysis proved. Fig. 1 presents the granulometric distributions of the lime and aggregate, respectively. The selected binder: aggregate ratio (B:Ag) was 1:1, by volume. This decision was taken in accord with previous data [17,18]. Volume proportions were converted into weight in order to avoid any imprecise measurement (Table 1). Three different dry mixtures were prepared. One of them was composed only of lime and aggregate, and was taken as a reference mortar. One only additive was incorporated in each one of the remaining mortars, in order to check clearly its possible efficiency, avoiding other variables. For each additive, a dosage of 0.06% of the total dried mortar's weight was incorporated. This dosage was selected in line with those used in previous studies [1,5–7]. The additives used were obtained from a supplier as commercial products: hydroxypropyl methylcellulose (HPMC) HK 15 M from Hercules and a guar gum derivative (GG), whose chemical composition was hydroxypropyl guaran, from Lamberti Quimica S.A. (ESACOL HS-30®). This latter substance is the hydroxypropyl derivative of the guaran, a polygalactomannan heteropolymer formed by units of mannose linearly linked, with lateral links of galactose, with a ratio of 2:1 mannose:galactose [19]. The criteria for this choice were that HPMC was one of the most widespread water-retaining and viscosity-enhancing admixture in cement materials and that the guar gum derivative has been widely used in dietetics and pharmacy [20,21] due to its ability to increase viscosity, but its potential as admixture for mortars has received scant attention [22,23]. This last substance is now being marketed for both cement and aerial lime based materials.

## 3. Methods

### 3.1. Mortar preparation

The amount of water was set in order to achieve a mortar flow of  $160 \pm 10$  mm after the flow table test. This value allows us to obtain similar workability for all the tested mixtures [17].

The mixer was a Proeti ETI 26.0072. Lime, aggregate and additive (when necessary) were blended for 90 s at low speed. Water was then added and mixed for a further 90 s at low speed. Mortars settled for 10 min before being tested, to let the additive take effect. Straight afterwards, the properties of the fresh mixtures were determined as described below. Table 1 shows the composition of the three different mixtures.

For hardened mixture tests, mortars were moulded in prismatic  $40 \times 40 \times 160$  mm casts and demoulded 5 days later [24]. Pastes were compacted in a specific device for 60 s. Curing was executed in ambient laboratory conditions until the test day ( $\text{RH } 60 \pm 10\%$  and  $20 \pm 5^\circ\text{C}$ ). A total of 15 specimens was prepared for each mixture; hence, 45 specimens were studied. Different curing times were set: 7, 28, 91, 182 and 365 days; three specimens of each mortar were tested at each curing time, and the reported results are an average of all these.

### 3.2. Rheological properties

For the fresh mixtures, consistency [25], density [26], air content [27], water-retention capacity [28] and open time [29] were measured.

Viscosities of lime pastes and water solutions with GG or HPMC were determined using a HAAKE Viscotester VT 550, with a programme of rotation speeds varying from 1.5 to 510 s<sup>-1</sup> during 5.5 min. In addition, viscosities at low shear rate (5 s<sup>-1</sup> for 20 min) were also determined. Four different water solutions of each one of the additives (HPMC and GG) were prepared as follows: 98 g of water were put into four glass containers. The pH was then adjusted to 7 (two solutions) or 13 (two solutions) by NaOH additions. The ionic strength was then modified in two solutions by adding enough NaCl to achieve a concentration 1 M. In the other two solutions, NaCl was not added. Finally, 2 g of the additive were added and the solution was stirred manually for one minute before being measured. The lime pastes were prepared according to the amounts set in Tables 2 and 3 shows the detailed programme of rotation speeds.

### 3.3. Hardened mixture properties

At hardened state, analysis of density, water absorption through capillarity [30], water vapour permeability [31], shrinkage and pore size distribution (by means of mercury intrusion porosimetry) were carried out. Furthermore, different test specimens were prepared in order to study the mechanical strength at different times (from 7 to 365 days). The degree of carbonation was also assessed by means of thermogravimetric analysis (TG) at these different times. TG was conducted using a simultaneous TGA–sDTA 851 Mettler Toledo thermoanalyser, with alumina crucibles, fitted with holed lids, at a 20 °C min<sup>-1</sup> heating rate, under static air atmosphere, from ambient temperature to 1150 °C. The weight loss at ~450 °C was attributed to the Ca(OH)<sub>2</sub> dehydroxylation, while the weight loss at ca. 800 °C was related to the CaCO<sub>3</sub> decarbonation [32]. Durability was also studied through freezing–thawing cycles.

#### 3.3.1. Mechanical strengths

The three-point flexural tests were carried out in the mortar specimens using a Frank/Controls 81565 compression machine at low rates of loading (10 N s<sup>-1</sup>). Flexural strength determination was performed on the Ibertest IB 32-112V01. Compressive strength tests were executed on the two fragments of each specimen resulting from the flexural tests. This was carried out on a Proeti ETI 26.0052, and the rate of loading was 50 N s<sup>-1</sup>.

#### 3.3.2. Density and shrinkage

The specimens used for tests of shrinkage and density in hardened mixtures were those prepared for determining mechanical strengths. Before the specimens were broken during the mechanical test, their length was measured with a gauge and the mass was set with a balance.

**Table 2**  
Composition of lime pastes for viscosity studies.

	Composition (g)			
	Lime	HPMC	GG	Water
<i>Lime pastes</i>				
REF	25	–	–	25
Lime + HPMC	25	0.5	–	25
Lime + GG	25	–	0.5	25

**Table 3**  
Shear rates measured in the viscotester.

Step	Time (s)	Shear rate (s <sup>-1</sup> )
1	30	1.5
2	30	3.1
3	30	5.1
4	30	10.2
5	30	51.1
6	30	102
7	30	153
8	30	170
9	30	306
10	30	340
11	30	510

#### 3.3.3. Pore structure

The pore size distribution test was performed by using a Micromeritics AutoPore IV 9500 with a pressure range between 0.0015 and 207 MPa. Pressure, pore diameter and intrusion volume were automatically registered. Open porosity was also determined according to the water saturation test with a hydrostatic balance [33].

#### 3.3.4. Durability: freezing–thawing cycles

In order to test the performance of the additives, specimens with the set dosage of admixtures were subjected to durability cycles and compared to a control group. Mortars were prepared as aforementioned in 3.1. Curing was executed in ambient laboratory conditions over 56 days (RH 60 ± 10% and 20 ± 5 °C), and after that, samples were subjected to several freezing–thawing cycles. They were immersed in water until complete saturation (24 h) and then frozen in a freezer at (–10 ± 2 °C) (24 h). Table 4 shows the characteristics of the set cycles. A total of ten specimens were prepared for each mixture, so 30 specimens were studied. Different testing days were set corresponding to 1, 4, 7, 10 and 14 complete cycles. The qualitative evaluation was visually determined, using a previously reported criterion [34], which attributes degree 0 of alteration for samples without evidence of decay; degree 1 for slightly altered samples, with some thin and short cracks at the surface of the specimens; degree 2 for altered samples, showing several deeper cracks (like spider's web); degree 3 for heavily altered specimens which had deep cracks and were undergoing swelling; degree 4 for a severe decay, large and deep cracks, large swelling of the specimen and a partial weight loss; and, finally, degree 5 for completely destroyed samples, with only parts remaining.

Compressive strengths were also determined on the different testing days. Two specimens of each mortar were tested at each point, and the reported results are an average of the two.

## 4. Results and discussion

### 4.1. Rheological properties

#### 4.1.1. Amount of required water and consistency

In the present study, the flow value had previously been set, so Table 1 shows the amount of water that the addition of the two admixtures required to reach that value. In both cases, a large amount of water was needed in order to achieve the set flow,

**Table 4**  
Procedure for freeze–thaw cycling.

Cycle duration	Steps	Temperature (°C)	Water immersion	Time (h)
48 h	Step 1	Room temperature	Yes	24
	Step 2	–10 ± 2	No	24

especially for the HPMC sample (ca. 22% more mixing water than the reference mortar). These results are in agreement with those obtained in lime mortars by Seabra et al. [7] In the present study, the flow was set within a range ( $160 \pm 10$  mm), so the amount of water necessary in order to reach this flow rose in the presence of the additives.

#### 4.1.2. Density

A decrease of 5.1% for HPMC and 3.8% for GG in density of the fresh mixtures was observed compared to the reference mixture. The more water was added, the lower the density that was achieved (Table 5). These results echo those of Paiva et al. [1] and Seabra et al. [7], who reported that the incorporation of HPMC in both cement mortars and lime mortars led to a decrease in fresh density.

#### 4.1.3. Air content

As Table 5 shows, the incorporation of the additives led to a larger air content: 3.4% of entrained air was determined when HPMC was added, while 5.0% of entrained air when the admixture was GG. An increase of entrained air compared to the result of the reference mixture (2.8%) was thus determined, being more noticeable when GG was used. In order to give an explanation for this air-entraining ability, the chemical composition of these admixtures should be considered. In fact, these water-soluble synthetic and natural organic polymers (like HPMC or guar gum) have inherent surfactant properties that lower the surface tension of the aqueous phase of the paste, giving rise to air entrainment [15].

Previous studies on cement mortars [1,23] and on lime mortars [7] have shown that water-retaining agents based on cellulose ethers entrain large volumes of air.

The studied additives clearly induced an air content increase. This air content could enhance the durability of the material in the face of freezing–thawing cycles if the amount of entrained air was not too large. This fact might be due to the voids generated that provide an escape boundary to which water can flow and freeze [35].

#### 4.1.4. Water-retention capacity

The results of water-retention capacity showed high values, above 90%, for all the mortars (Table 5). The small particle size of the calcium hydroxide, and hence its specific surface area, allow the lime to act as a very retentive material [7,36]. This fact can explain the large water retention value found for the plain lime mortar (94.3%). However, the influence that each additive had on this property was very different: while GG behaved raising the

water-retention capacity of the mortar (98.4%), HPMC led to a lower value (91.9%) than the reference. This was a surprising result, since cellulose ethers usually achieve water retention capacities higher than 99% in cement-based mortars [1], which have themselves lower retention capacity than lime materials.

In spite of the fact that the addition of HPMC required a larger amount of mixing water than the addition of GG (11.1% of increase), HPMC mortar showed the lowest value of retained water. This issue made it clear that the two studied admixtures behaved differently. In order to elucidate factors affecting such a different performance between GG and HPMC, a discussion is included in Section 4.1.6.

#### 4.1.5. Setting time

As reported in the Introduction, the setting mechanism in aerial lime-based mortars is described by the carbonation process. An excess of either mixing water (both HPMC and GG additions required large amount of mixing water) or water-retention capacity could be detrimental to the setting of the aerial lime mortars. The obtained results showed a dramatic increase in the setting time when any of the additives was added to the mixtures: setting time ranged from 195 min for the reference mortar to 630 min for HPMC mortar or 870 min for GG mortar (Table 5).

The influence of the water retention capability turned out to be greater in prolonging the setting time than the effect of an excess of mixing water. Samples with GG, with the highest water-retention capacity, showed the longest setting time while the largest amount of mixing water was required for HPMC mixtures.

In order to assess the influence that both additives had on the carbonation process, the amount of free water,  $\text{Ca(OH)}_2$  and  $\text{CaCO}_3$  over time were determined by means of TG analysis (Table 6). The effect of mixing water excess in the HPMC sample still remained at 7 days, clearly hindering the carbonation (18.72% of  $\text{Ca(OH)}_2$ ). The influence of both the mixing water and the retained water in the GG samples also had an effect, but to a lesser extent, at 7 days (lower amount of uncarbonated  $\text{Ca(OH)}_2$  – 14.15% – and a larger amount of  $\text{CaCO}_3$  – 80.68% –). At 28 days, only slight differences in the carbonation as well as in the amount of free water were found. At 91 days no significant differences were detected.

This evolution of carbonation meant that both the excess of mixing water and the water retaining capacity of the additives had a clear influence on the setting time for fresh mixtures, as proved by its strong delay. Only an excessive amount of mixing water had a clear influence on the carbonation at short term (see the above-mentioned results at 7 and 28 days), as was the case for the HPMC sample. The water retaining action of the GG, while it caused a long delay in the setting time, had, if any, little influence on the degree of carbonation in hardened mixtures. However, the delay in setting time is a drawback for application of lime mortars, as reported in the Introduction, so this issue could impose a strong limitation on the use of these additives in aerial lime mortars.

#### 4.1.6. Behaviour of GG and HPMC-modified mortars

The viscosity enhancing behaviour of water soluble polymers in binding materials is closely related to their water retaining action

**Table 5**  
Properties of the three mortars.

	Density (g/L)	Air content (%)	Water-retention capacity (%)	Setting time (minutes)
REF	1942.5	2.8	94.3	195
HPMC	1842.5	3.4	91.9	630
GG	1869.6	5.0	98.4	870

**Table 6**  
Results of the TG analyses: compositional data (%) of free water, calcium hydroxide and calcium carbonate in hardened mixtures after different curing durations.

	Curing time (days)								
	7			28			91		
	H <sub>2</sub> O (%)	Ca(OH) <sub>2</sub> (%)	CaCO <sub>3</sub> (%)	H <sub>2</sub> O (%)	Ca(OH) <sub>2</sub> (%)	CaCO <sub>3</sub> (%)	H <sub>2</sub> O (%)	Ca(OH) <sub>2</sub> (%)	CaCO <sub>3</sub> (%)
REF	0.58	14.54	80.91	0.57	12.97	82.95	0.39	5.70	89.77
HPMC	1.28	18.72	75.95	0.67	14.41	80.68	0.36	5.83	90.45
GG	0.61	14.15	80.68	0.57	14.23	81.59	0.37	6.36	89.54



[23]. A thorough discussion on the factors affecting the viscosity of the mixtures with these admixtures is therefore necessary. In addition, the performance in terms of viscosity along with water retention capability has been reported to be substantially different in cement-based mortars than in the results of the present work. Moreover, the differences in the experimental values between HPMC and GG specimens need to be explained.

Both cement and lime media are characterized by large pH values (around 12–13) and high ion concentrations, as Table 7 shows through the evolution of the pH and conductivity values in cement and lime solutions. The values refer to the beginning of the setting process, when viscosity-enhancing admixtures (water retainers) are supposed to exert their role.

Viscosity of the solutions with different pH values and ionic strength was determined in order to test the behaviour of GG and HPMC. Fig. 2 shows the results obtained by monitoring the change in strain over time in response to fixed values of applied stress.

The flow curves showed an obvious shear-thinning behaviour, i.e. reduction in viscosity with increasing shear rate. The influence of the pH increase on the viscosity values was also clear: a reduction in viscosity when pH values rose from 7 to 13 was obtained in both HPMC and GG solutions.

It is possible to suggest a general explanation for this fact: the addition of alkali gives rise to ionization of hydroxyl groups (from  $\text{OH}^-$  to  $\text{O}^-$ ). As a result, electrostatic repulsions between chains of the polymer appear, thus inhibiting intermolecular association and hence reducing viscosity [37]. With respect specifically to GG, it has been stated that alkaline medium causes a drop in viscosity owing to the inhibition of the hyperentanglement (association of unsubstituted mannan sequences in the galactomannan chains). This last mechanism has been proposed to explain the decrease in viscosity rather than the degradation and subsequent molecular weight reduction induced under alkaline conditions by a “peeling” reaction [38]. On the other hand, HPMC showed negligible degradation in alkaline media [2].

Taking into account the effect of ionic strength, the addition of 1 M NaCl caused a viscosity reduction in both neutral and alkaline media. A reduction in the viscosity of poly-electrolytes on addition of salt at low polymer concentrations, and an increase at higher concentrations, have been frequently observed and explained by suppression of electrostatic repulsions between chain segments, i.e. non-specific charge screening [37]. At low polymer concentrations the decrease in repulsion between segments of the same chain could reduce the coil dimensions and hence the viscosity values.

Furthermore, an electrolyte can salt out a polymer from its solution, because ions have a greater affinity for water than the polymer, thus removing water from the polymer and dehydrating it. The loss of water of hydration is accompanied by a drop in relative

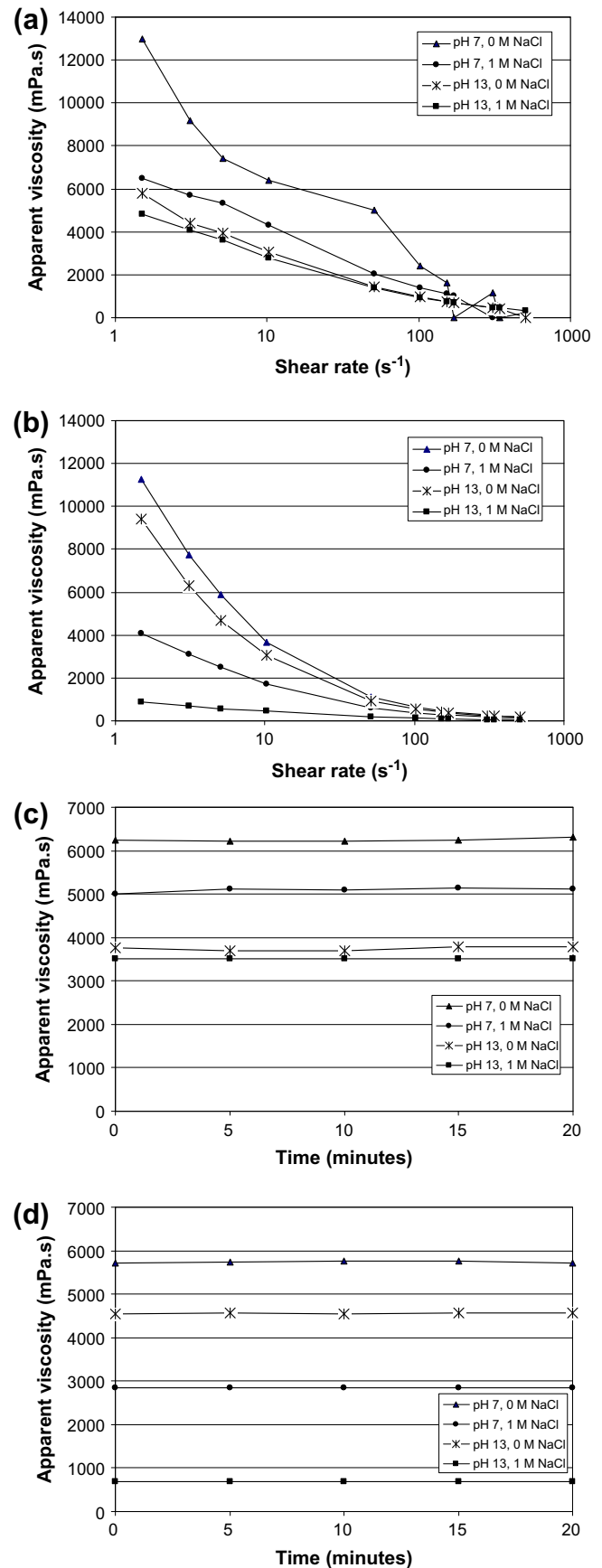


Fig. 2. Apparent viscosity results in water solutions with different pH/ionic strength values: (a) flow curve of HPMC vs. shear rate; (b) flow curve of GG vs. shear rate; (c) HPMC vs. time at low shear rate; (d) GG vs. time at low shear rate.

**Table 7**  
pH and conductivity evolution of cement and lime solutions (5% w/w of binding material) during 120 min.

Time (min)	pH		Conductivity (mS cm <sup>-1</sup> )	
	Cement	Lime	Cement	Lime
0	12.12	12.25	4.05	9.25
15	12.12	12.30	4.89	9.14
30	12.11	12.16	5.46	9.10
45	12.16	12.20	6.10	9.06
60	12.09	12.09	6.75	9.02
75	12.11	12.10	7.52	8.99
90	12.09	12.14	8.05	8.96
105	12.05	11.90	8.54	8.93
120	12.15	12.08	8.98	8.93

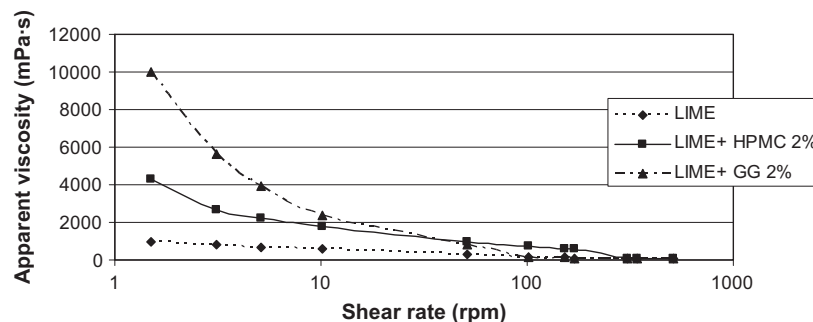


Fig. 3. Apparent viscosity vs. shear rate for lime pastes.

viscosity, but if the polymer loses more water of hydration, some polymer–polymer interactions would take place (especially between hydrophobic segments) giving rise to a dramatic increase in viscosity [39].

The joint effect of these two factors, alkaline pH and large ionic strength, gave rise to the sharpest drop in viscosity. However, GG underwent a more intense reduction than HPMC. This fact could be related to the structure of these two polymers. GG has a greater number of hydroxyl groups, which become ionized in alkaline conditions, increasing the electrostatic repulsions between chains, and thus reducing the hyperentanglement. Therefore, the viscosity of the solution decreased. Moreover, the large ionic strength played a role in this viscosity reduction in a way that is not well understood, perhaps by dehydrating the polymer. HPMC, with fewer hydroxyl groups and with more hydrophobic substituents, did not undergo such a dramatic drop in viscosity, because it was able to maintain the entanglement between different chains. HPMC would not be able to fix as many counterions as GG, owing to its lower charge density, which allows it to absorb the effect of ionic strength.

Taking into account all these factors, the high efficiency of HPMC as a VEA in cement mortars can be easily inferred [1–7].

Nevertheless, when slaked lime was added, this relationship between HPMC and GG was inverted. As Fig. 3 shows, GG led to larger viscosity values than HPMC, matching the water retention ability results (Table 5). The only difference with respect to the previously studied conditions was the presence of the slaked lime, because pH values and large ionic strength were maintained, so an explanation for the change in behaviour induced by great amounts of  $\text{Ca}(\text{OH})_2$  must be proposed.

Previous studies have emphasised the great ability of cellulose ethers to be adsorbed on  $\text{Ca}(\text{OH})_2$  crystals [40]. In lime-based mortars, the extremely large amount of  $\text{Ca}(\text{OH})_2$  crystals would provide a huge number of points where the HPMC could be adsorbed, thus decreasing the entanglement between different chains and producing a drop in viscosity results and a reduction in its water binding capacity. This adsorption could also be responsible for the low amount of entrained air found when HPMC was added (Table 5). Owing to the greater amount of ionized groups in such alkaline conditions, GG may show little likelihood of being adsorbed on neutral

surfaces, thus allowing the polymer chains to maintain to a certain extent the hyperentanglement and, as a consequence, the viscosity of the paste, especially considering that the ionized groups of GG may facilitate the entanglement between chains by a cross-linking phenomenon with  $\text{Ca}^{2+}$  ions [41]. For HPMC, Pourchez et al. [2] stated no calcium binding capacity, showing the different behaviour in the face of lime pastes between HPMC and GG.

## 4.2. Hardened mixture properties

### 4.2.1. Density

As Table 8 shows, the incorporation of any of the tested additives led to a reduction in the density of the material (from  $1.67 \text{ g mL}^{-1}$  of reference sample to  $1.58 \text{ g mL}^{-1}$  of both GG and HPMC specimens). This decrease in density can be explained as a result of the excess of mixing water, which increases the number of pores when it evaporates during the hardening process [17].

### 4.2.2. Shrinkage

The shrinkage coefficient of modified mortars was higher than that for the reference ( $13.59 \text{ mm m}^{-1}$  for the reference mortar, while 26.77 and 16.35 were determined for HPMC and GG samples, respectively). These high shrinkage coefficients can also be attributed to the large amount of mixing water [42,43]. It must be taken into account that lime mortars, in general, have been reported to show large shrinkage coefficients [40]. In accord with the values of the excess of mixing water, the HPMC mortar showed an extremely high value.

### 4.2.3. Water absorption capacity through capillarity

Water absorption is an important property for mortars, as they are usually exposed to environmental phenomena – such as rain – or in contact with elements that could be wet (soil). If the mortar absorbs water easily, it will become damaged and water movement inside the building structure will affect and damage other materials such as stones, through efflorescence phenomena [44].

In the present study, results for HPMC mortar showed higher water absorption through capillarity than for the reference. In contrast to this, GG mortar improved as far as this property was concerned (Table 8). Paiva et al. [1] reported that the water-retaining agents decreased the capillarity in cement mortars, and they related this behaviour to the fact that these admixtures entrap air, thus introducing small pores which could be able to cut the capillary network. In the present study, guar gum improved the water absorption due to the large air content in GG mortars after the mixing process.

### 4.2.4. Water vapour permeability

Water vapour permeability is another important property for avoiding damage caused by humidity. Mortars must have a substantial permeability level up to a point, to allow water vapour

**Table 8**  
Density, shrinkage, capillarity and permeability coefficients of hardened mortar samples.

	Density (g/mL)	Shrinkage coefficient (mm/m)	Capillarity coefficient (kg/m <sup>2</sup> min <sup>1/2</sup> )	Permeability coefficient
REF	1.67	13.59	2.36	16.6
HPMC	1.58	26.77	2.73	12.6
GG	1.58	16.35	1.96	15.0

to pass from the inside part of the building to the outside, avoiding retentions in the material. These retentions could be the cause of efflorescences and related problems [10,45].

The permeability coefficient expresses the difficulty that water vapour molecules have when trying to pass through mortar. A low coefficient implies high permeability.

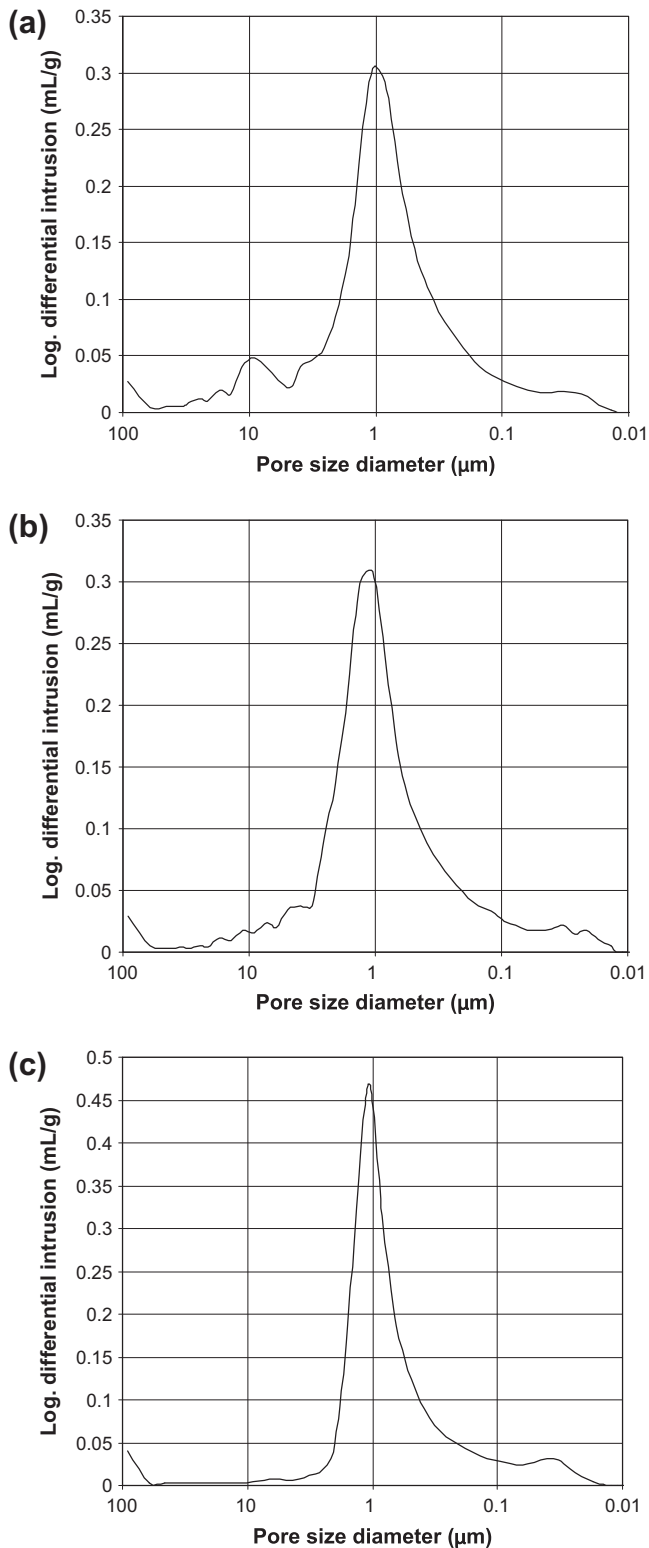


Fig. 4. Results from mercury intrusion porosimetry for the studied mortars; (a) REF; (b) HPMC; (c) GG.

Table 8 shows that both admixtures increased permeability, especially HPMC. When these results are compared with water absorption capacity through capillarity data, various hypotheses could be defended. First of all, it must be noted that water vapour molecules are much smaller than liquid ones, so some pores could be enough to allow water vapour to pass through, but not to absorb liquid water.

GG could thus change the mortar pores in such a way that very few remain interconnected and enable permeability, but these are not big enough to absorb water through capillarity. It could be said that GG decreases the number of macropores and mesopores and increases the number of micropores.

However, the incorporation of HPMC led to a light increase in capillarity and to a considerable rise in permeability, thus suggesting a larger number of micropores and macropores. Owing to the large amount of kneading water, evaporation during the hardening process could explain this behaviour.

#### 4.2.5. Pore structure

Fig. 4 shows the results obtained for the mortars studied after 91 days of curing. All of them showed a main peak – almost unimodal distribution – corresponding to 1  $\mu\text{m}$  diameter pores, which was in accordance with previous work on lime-based mortars [44,46,47]. The addition of GG led to a drastic reduction in the percentage of the small peaks related to larger pores (diameters from

Table 9  
Open porosity values (%) vs. curing time of the hardened mixtures.

	Curing time (days)				
	7	28	91	182	365
REF	32.73	34.38	33.08	33.72	33.84
HPMC	37.16	35.73	36.64	33.02	35.92
GG	35.89	34.66	34.84	35.85	34.98

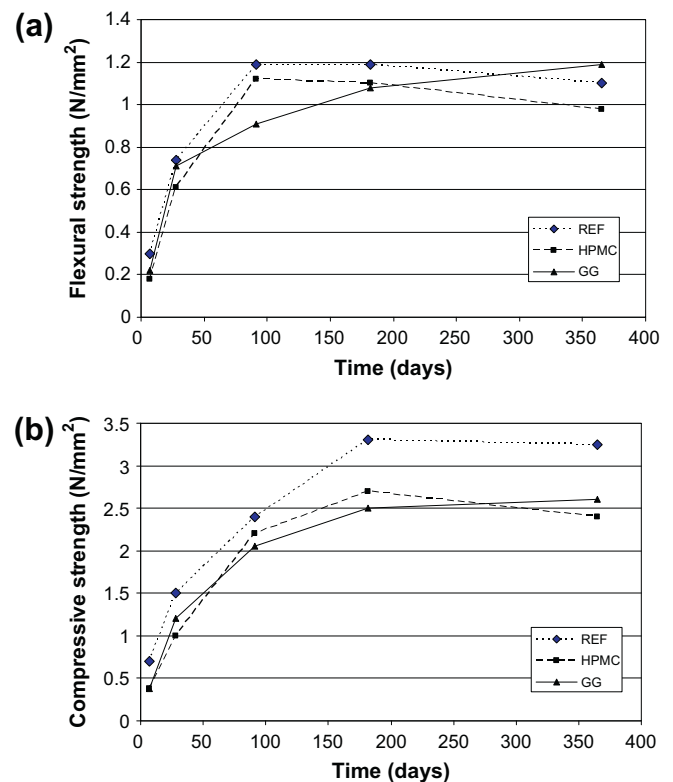


Fig. 5. Flexural and compressive strength vs. time for the tested mortars.

100  $\mu\text{m}$  to 10  $\mu\text{m}$ ), which almost disappeared, and to a considerable increase in the volume of intruded mercury at the main peak, which is sharper. This fact was also reflected in previously reported data [48]. Furthermore, the mortar containing GG slightly shifted this main peak towards higher values, but with a slight reduction in the AUC (area-under-curve). These results mean that the presence of this admixture contributed to blocking the larger pores and, at the same time, to making the smaller ones slightly larger, producing a more uniform pore size distribution characterized by

a higher pore diameter. This is in agreement with the conclusions deduced from capillarity and permeability data (Sections 4.2.3. and 4.2.4).

This pore size distribution, with lower porosity at larger sizes, may also explain the reduction of water absorption through capillarity, due to the high air content: air bubbles might cut off the capillary network, giving rise to a decrease in larger pores.

HPMC mortar showed a less pronounced reduction in the percentage of large pores between 100 and 10  $\mu\text{m}$  than GG mortar.

**Table 10**

Qualitative evaluation and weight changes of the mortars after freezing–thawing cycles.

	Freezing–thawing cycles									
	1 Cycle		4 Cycles		7 Cycles		10 Cycles		14 Cycles	
	AD	WC	AD	WC	AD	WC	AD	WC	AD	WC
REF	0	+17.6	4	+18.5	–	–	–	–	–	–
HPMC	0–1	+23.3	1–2	+27.8	5	–	–	–	–	–
GG	0	+21.1	2–3	+17.8	4–5	+23.7	–	–	–	–

AD: Alteration degree.

Assignment of alteration degrees:

0: Without alteration.

1: Slightly altered, with some small (thin and short) cracks on the surface of the specimens.

2: Altered, with several web like and deeper cracks.

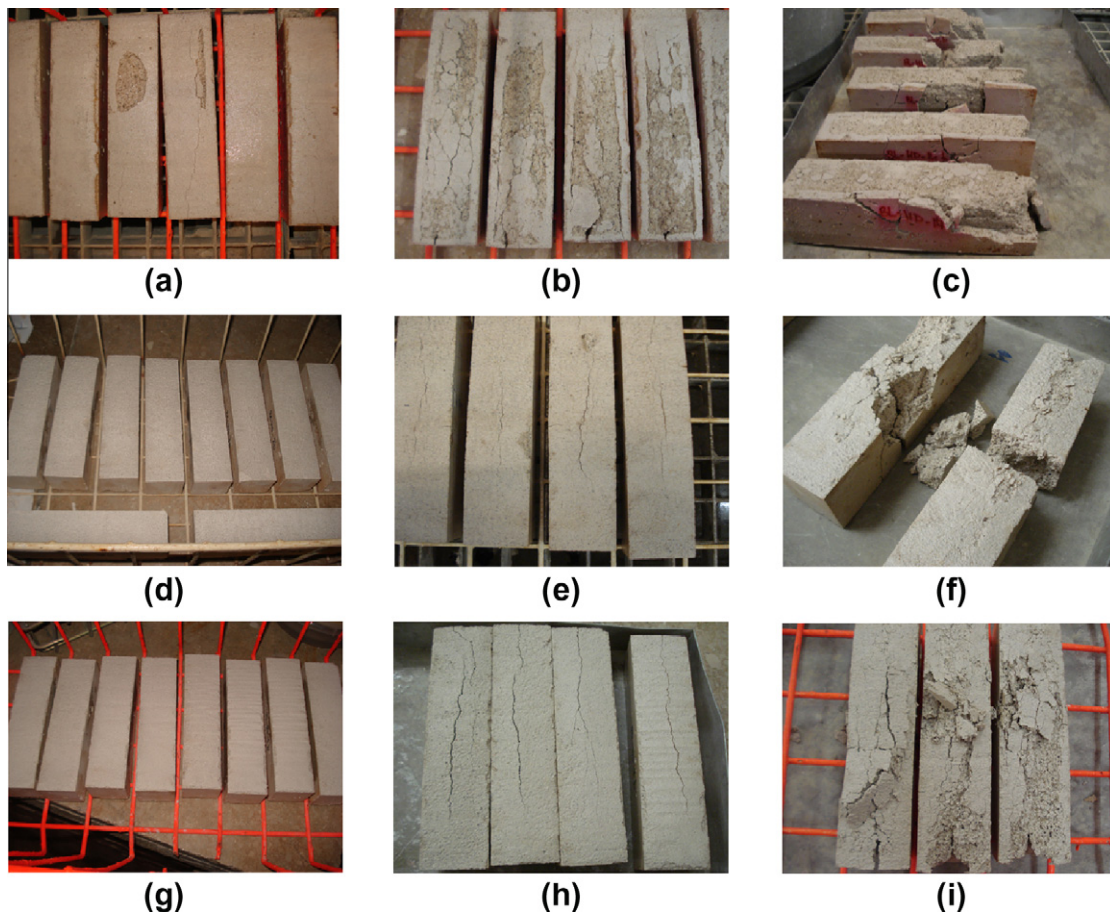
3: Very altered, with several deep cracks and swelling of the specimen.

4: High degree of alteration, with large and deep cracks, and large swelling of the specimen including a partial weight loss.

5: Completely altered. The specimen is practically destroyed, with only small pieces intact.

WC: Weight changes. Percentage of weight variation of the original hardened samples.

– : not determined as the specimens were completely destroyed.



**Fig. 6.** Tested specimens after freezing–thawing cycles; (a) REF samples after 1 cycle; (b) REF samples after four cycles, with clear evidences of alteration; (c) REF samples totally destroyed (after 6 cycles); (d) HPMC specimens after 1 cycle; (e) HPMC specimens after 4 cycles, with slight signs of deterioration; (f) destroyed HPMC specimens (after 7 cycles); (g) GG samples after 1 cycle; (h) GG mortars after 4 cycles, with signs of alteration; (i) GG samples totally deteriorated (after 8 cycles).



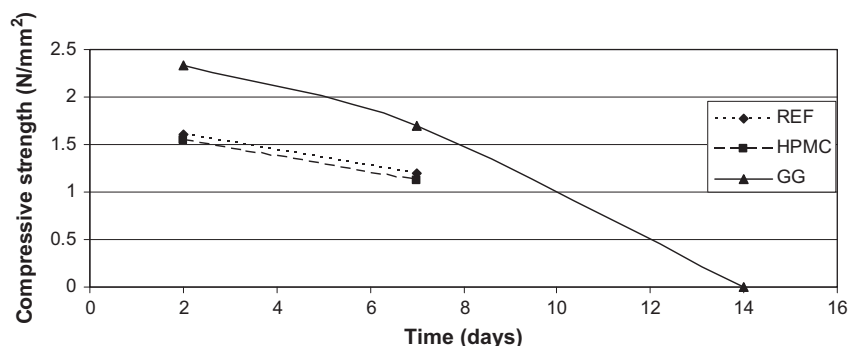


Fig. 7. Compressive strength of the mortars after freezing–thawing tests.

The AUC at the main peak was almost the same as the reference. As in GG mortar, this peak appeared to have shifted slightly toward higher values. Owing to the presence of a certain number of large pores, water absorption through capillarity was not improved by the use of this additive. The rise in water vapour permeability might be related to a better interconnection between the existing small pores (as a result of the smaller amount of entrapped air).

Open porosity was also evaluated over time (Table 9). HPMC and GG mortars gave rise to larger values than the reference mortar on the test days. The excess of mixing water together with the entrained air can explain this increase in the open porosity when additives were added, which, as explained below, was useful to interpret the compressive strength results.

#### 4.2.6. Mechanical strengths

Fig. 5 shows the mechanical behaviour of the studied mortars, in terms of flexural and compressive strengths. As expected for lime-based mortars, maximum mechanical strengths were reached after a long period of time. The addition of the studied admixtures was, as a whole, detrimental to the compressive strength. In the short term, some degree of hindrance of the carbonation process must be taken into account (as explained in Section 4.1.5). In addition, the excess of mixing water and its retention could also give rise to a decrease in strength. The larger open porosity of the modified mortars also tended to support these events.

In cement mortars, the influence of organic water retainers on mechanical strengths is not very clear. Paiva et al. [1] found a decrease in mechanical properties associated with the incorporation of this kind of additive, and explained this behaviour through the observed increase in porosity and the related decrease in density. In the present study, the same arguments could be brought to bear: both admixtures produced a decrease in the density of hardened material. However, Mishra et al. [5] reported a rise in mechanical strengths when water-retaining agents were used in cement mortars. In their work, maximum mechanical strengths were reached over a longer period of time owing to the induced delay, but once they were reached, the values were higher than the reference ones. In the present work, because of the lack of hydraulic components in the studied materials, the presence of water in excess was not positive for the final properties of the mortars (Section 4.1.5).

Furthermore, HPMC and especially GG, produced an increase in the air content of the mortars. As explained in Section 4.1.3, excessively large amounts of entrapped air could lead to undesirable consequences, one of the main ones being the reduction in mechanical strengths [1,49]. Fig. 5 shows a drop in the compressive strength of GG and HPMC mortars.

#### 4.2.7. Durability: freezing–thawing cycles

Table 10 shows the degree of alteration and weight variation of the mortars after they were subjected to several freezing–thawing

cycles. Weight variations were strongly related to the open porosity values: the larger the open porosity, the higher the water absorption and therefore the weight increase. Not all the prepared mortars lasted long enough to be tested at the set times, as can be seen in Fig. 6.

Only two mechanical data were measured for the reference material, as all the specimens were destroyed after 6 cycles (Fig. 6). They showed signs of deterioration from the first stages of the exposure onwards. Mortars with HPMC lasted one cycle longer, but they were broken before being measured. Although the duration of the test was the same for both materials, their evolution was very different. As can be observed in Fig. 6, samples with HPMC started to show major deterioration several cycles later than the reference mortar. The deterioration levels of GG mortars were different at some stages. In addition, compressive strengths were clearly higher than the other tested materials, and could also be measured after 7 cycles, even when the specimens were so weak that they broke before the result was detected (Fig. 7). As mentioned above (Section 4.1.3), the large air content of this mixture could be the reason why durability improved, as air voids allow the water to expand during the freezing process without damaging the structure [35].

## 5. Conclusions

HPMC and the guar gum derivative were tested as additives for lime-based mortars and different properties were studied in fresh mixtures as well as in hardened material, in order to test their performance.

At the studied dosage, both additives required a larger amount of water than the reference material to obtain the same consistency. This excess of mixing water hindered the carbonation process in the short term and increased the total porosity of the modified mortars, thus being detrimental to a certain extent to the compressive strength of the hardened specimens.

Although the amount of mixing water was the greatest when HPMC was added, this additive did not raise the water-retention capacity of the fresh mixtures. In addition, several data, such as high water absorption through capillarity, high permeability and a long delay in setting time, meant that this additive resulted in an undesirable general performance.

Furthermore, in contrast to the well-known effect of HPMC in cement-based materials, its viscosity enhancing behaviour in aerial lime mortars turned out to be very limited. The presence of large amounts of slaked lime proved to be conclusive to explain the fact that HPMC could adsorb onto calcium hydroxide crystals, thus reducing its entanglement between chains and hence the viscosity of the pastes, its water retention ability and the entrapped air.

On the other hand, GG, which had a larger quantity of ionized groups at alkaline pH, owing to its large charge density, reduced

its adsorption capacity onto  $\text{Ca}(\text{OH})_2$  particles. The ionized groups made it possible to increase the GG ability for calcium binding, giving rise to a viscosity increment through a cross-linking phenomenon.

This viscosity enhancing action could be very useful in order to improve aerial lime mortars (for rendering purposes, as just one example). The air content increased in mortars modified by GG, changing the pore size distribution and giving rise, as a consequence, to some positive aspects such as a decrease in water absorption and an improvement in durability through freezing–thawing cycles. However, some non-desirable effects related to its water retaining action, such as the delay in setting time, must be taken into account as they may affect its performance negatively.

With a view to using the guar gum derivative in aerial lime mortars, further studies will be necessary (i) to adjust the dosage in order to reduce the mixing water requirements and (ii) to combine it with other admixtures that could be helpful to overcome the drawbacks connected with the setting time delay.

## Acknowledgements

The authors want to thank CTH Navarra and Fernando Moreno (Calinsa S.A. Navarra) for the material supplied. We are also grateful to the staff in Laboratorio de Edificación (Universidad de Navarra) for their material support and invaluable help. This work has been funded by the Ministry of Education and Science of Spain (MAT2007-65478) and FUNA (Fundación Universitaria de Navarra).

## References

- [1] Paiva H, Esteves LP, Cachim PB, Ferreira VM. Rheology and hardened properties of single-coat render mortars with different types of water retaining agents. *Constr Build Mater* 2009;23:1141–6.
- [2] Pourchez J, Govin A, Grosseau P, Guyonnet R, Guilhot B, Ruot B. Alkaline stability of cellulose ethers and impact of their degradation products on cement hydration. *Cem Concr Res* 2006;36:1252–6.
- [3] Pourchez J, Peschard A, Grosseau P, Guyonnet R, Guilhot B, Vallee F. HPMC and HEMC influence on cement hydration. *Cem Concr Res* 2006;36:288–94.
- [4] Seabra MP, Labrincha JA, Ferreira VM. Rheological behaviour of hydraulic lime-based mortars. *J Euro Ceram Soc* 2007;27:1735–41.
- [5] Mishra PC, Singh VK, Narang KK, Singh NK. Effect of carboxymethyl-cellulose on the properties of cement. *Mater Sci Eng A* 2003;357:13–9.
- [6] Singh NK, Mishra PC, Singh VK, Narang KK. Effects of hydroxyethyl cellulose and oxalic acid on the properties of cement. *Cem Concr Res* 2003;33:1319–29.
- [7] Seabra MP, Paiva H, Labrincha JA, Ferreira VM. Admixtures effect on fresh state properties of aerial lime based mortars. *Constr Build Mater* 2009;23:1147–53.
- [8] Jolicoeur C, Simard MA. Chemical admixture–cement interactions: phenomenology and physico-chemical concepts. *Cem Concr Compos* 1998;20:87–101.
- [9] Malinowski R. Ancient mortars and concretes, durability aspects, mortars, cements and grouts used in conservation of historic buildings. In: *Proceedings of the symposium. Rome: ICCROM*; 1981. p. 341–50.
- [10] Mosquera MJ, Benitez D, Perry SH. Pore structure in mortars applied on restoration. Effect on properties relevant to decay of granite buildings. *Cem Concr Res* 2002;32:1883–8.
- [11] Izaguirre A, Lanas J, Alvarez JL. Effect of water-repellent admixtures on the behaviour of aerial lime-based mortars. *Cem Concr Res* 2009;39:1095–104.
- [12] Izaguirre A, Lanas J, Alvarez JL. Behaviour of a starch as a viscosity modifier for aerial lime-based mortars. *Carbohydr Polym* 2010;80:222–8.
- [13] Rodriguez-Navarro C, Ruiz-Agudo E, Ortega-Huertas E, Hansen E. Nanostructure and irreversible colloidal behavior of  $\text{Ca}(\text{OH})_2$ : implications in cultural heritage conservation. *Langmuir* 2005;21:10948–57.
- [14] Arandigoyen M, Alvarez JL. Carbonation process in lime pastes with different water/binder ratio. *Mater Constr* 2006;56:5–18.
- [15] Rixom R, Mailvaganam N. Chemical admixtures for concrete. London: E&FN Spon; 1999. p. 214–5.
- [16] UNE-EN 459-1, Building lime. Part 1. Definition, specification and conformity criteria; 2001.
- [17] Lanas J, Alvarez JL. Masonry repair lime-based mortars: factors affecting the mechanical behaviour. *Cem Concr Res* 2003;33:1867–76.
- [18] Lanas J, Perez Bernal JL, Bello MA, Alvarez JL. Mechanical properties of masonry repair dolomitic lime-based mortars. *Cem Concr Res* 2006;36(5):951–60.
- [19] Mathur R, Bohra S, Mathur V, Narang CK, Mathur NK. Chiral ligand exchange chromatography on polygalactomannan (Guaran). *Chromatographia* 1992;33:336–8.
- [20] Funami T, Kataoka Y, Omoto T, Goto Y, Asai I, Nishinari K. Food hydrocolloids control the gelatinization and retrogradation behavior of starch. 2a. Functions of guar gums with different molecular weights on the gelatinization behavior of corn starch. *Food Hydrocolloids* 2005;19:15–24.
- [21] George M, Abraham TE. pH sensitive alginate-guar gum hydrogel for the controlled delivery of protein drugs. *Int J Pharm* 2007;335:123–9.
- [22] Pera J, Ambroise J. New applications of calcium sulfoaluminate cement. *Cem Concr Res* 2004;34:671–6.
- [23] Khayat KH. Viscosity-enhancing admixtures for cement-based materials – an overview. *Cem Concr Compos* 1998;20:171–88.
- [24] EN 1015-11: Methods of test for mortar for masonry – part 11: determination of flexural and compressive strength of hardened mortar.
- [25] EN 1015-3: Methods of test for mortar for masonry – part 3: determination of consistence of fresh mortar (by flow table).
- [26] EN 1015-6: Methods of test for mortar for masonry – part 6: determination of bulk density of fresh mortar.
- [27] EN 1015-7: Methods of test for mortar for masonry – part 7: determination of air content of fresh mortar.
- [28] UNE 83-816-93, Test methods. Mortars. Fresh mortars. Determination of water retentivity.
- [29] EN 1015-9: Methods of test for mortar for masonry – part 9: determination of workable life and correction time of fresh mortar.
- [30] EN 1015-18: Methods of test for mortar for masonry – part 18: determination of water absorption coefficient due to capillary action of hardened mortar.
- [31] EN 1015-19: Methods of test for mortar for masonry – part 19: determination of water vapour permeability of hardened rendering and plastering mortars.
- [32] Arandigoyen M, Bicer-Simsir B, Alvarez JL, Lange DA. Variation of microstructure with carbonation in lime and blended pastes. *Appl Surf Sci* 2006;252:7562–71.
- [33] RILEM: Recommended tests to measure the deterioration of stone and assess the effectiveness of treatment methods. *Mater Struct* 1980;13:175–253.
- [34] Lanas J, Sirera R, Alvarez JL. Study of the mechanical behavior of masonry repair lime-based mortars cured and exposed under different conditions. *Cem Concr Res* 2006;36(5):961–70.
- [35] Chatterji S. Freezing of air-entrained cement-based materials and specific actions of air-entraining agents. *Cem Concr Compos* 2003;25:759–65.
- [36] Green KM, Carter MA, Hoff WD, Wilson MA. The effects of lime and admixtures on the water-retaining properties of cement mortars. *Cem Concr Res* 1999;29:1743–7.
- [37] Doyle JP, Lyons G, Morris ER. New proposals on “hyperentanglement” of galactomannans: solution viscosity of fenugreek gum under neutral and alkaline conditions. *Food Hydrocol* 2009;23:1501–10.
- [38] Goycoolea FM, Morris ER, Gidley MJ. Viscosity of galactomannans at alkaline and neutral pH: evidence of “hyperentanglement” in solution. *Carbohydr Pol* 1995;27:69–71.
- [39] Mitchell K, Ford JL, Armstrong DJ, Elliott PNC, Rostron C, Hogan JE. The influence of additives on the cloud point, disintegration and dissolution of hydroxypropylmethylcellulose gels and matrix tablets. *Int J Pharm* 1990;66:233–42.
- [40] Knapen E, Gemert DV. Cement hydration and microstructure formation in the presence of water-soluble polymers. *Cem Concr Res* 2009;39:6–13.
- [41] Perez-Mateos M, Montero P. Effects of cations on the gelling characteristics of fish mince with added nonionic and ionic gums. *Food Hydrocol* 2002;16:363–73.
- [42] Mesbah HA, Buyle-Bodin F. Efficiency of polypropylene and metallic fibres on control of shrinkage and cracking of recycled aggregate mortars. *Constr Build Mater* 2009;13:439–47.
- [43] Fernandes V, Silva L, Ferreira VM, Labrincha JA. Influence of the kneading water content in the behaviour of single-coat mortars. *Cem Concr Res* 2005;35:1900–8.
- [44] Arandigoyen M, Perez Bernal JL, Bello Lopez MA, Alvarez JL. Lime-pastes with different kneading water: pore structure and capillary porosity. *Appl Surf Sci* 2005;252:1449–59.
- [45] Maravelaki-Kalaitzaki P. Hydraulic lime mortars with siloxane for waterproofing historic masonry. *Cem Concr Res* 2007;37:283–90.
- [46] Collet F, Bart M, Serres L, Miriel J. Porous structure and water vapour sorption of hemp-based materials. *Constr Build Mater* 2008;22:1271–80.
- [47] Lanas J, Perez-Bernal JL, Bello MA, Alvarez Galindo JL. Mechanical properties of natural hydraulic lime-based mortars. *Cem Concr Res* 2004;34:2191–201.
- [48] Ouyang X, Guo Y, Qiu X. The feasibility of synthetic surfactant as an air entraining agent for the cement matrix. *Constr Build Mater* 2008;22:1774–9.
- [49] Saric-Coric M, Khayat KH, Tagnit-Hamou A. Performance characteristics of cement grouts made with various combinations of high-range water reducer and cellulose-based viscosity modifier. *Cem Concr Res* 2003;33:1999–2008.