Cement and Concrete Research 39 (2009) 573–579

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: http://ees.elsevier.com/CEMCON/default.asp

Effect of brief heat-curing on microstructure and mechanical properties in fresh cement based mortars

P. Ballester [a], A. Hidalgo [b], I. Mármol [a], J. Morales [c], L. Sánchez [c,]*

[a] Cementos Kola S.A. (CEMKOSA), Avda. Agrupación Córdoba no. 17, Córdoba, Spain
[b] Instituto Eduardo Torroja-CSIC, Madrid, Spain
[c] Departamento de Química Inorgánica, Facultad de Ciencias-Universidad de Córdoba. Campus de Rabanales, Edificio Marie Curie, 1407, Córdoba, Spain

ARTICLE INFO

Article history:
Received 21 February 2008
Accepted 22 April 2009

Keywords:
Mortar
Cement
Curing
Temperature

ABSTRACT

The effect of temperature on fresh mortar and cement paste was evaluated by simulating the curing conditions of external buildings plastering applied under extremely hot weather. The specimens were heated at controlled temperatures in the 40—80 °C range by exposure to IR radiation over short periods. The effect of soaking for a short time was also examined. The results of compressive strength tests, scanning electron microscopy, infrared spectroscopy and mercury porosimetry helped to characterize the mechanical and physico-chemical properties of the studied sample. Early age behaviour (28 days) in neat cement was barely affected by the temperature. By contrast, exposure to high temperatures caused significant microstructural changes in the mortar. However, successive soaking over short periods was found to reactivate the mechanism of curing and restore the expected mechanical properties. Based on the results, application of cement based mortar at high temperatures is effective when followed by a short, specific soaking process.

1. Introduction

The intrinsic properties of hardened cement based mortars are influenced by the initial curing conditions. Outdoor mortars under hot weather have been found to exhibit an abnormal mechanical behaviour relative to mortars tested under standard laboratory conditions. Thus, plastering buildings with cement based mortar in the summer time in some places is discouraged, particularly in towns where temperatures near 50 °C can be easily reached.

The clearly deficient properties of the previous mortars are a matter of concern for both users and producers. In spite of manufactures' recommendations [1], bricklayers irrigate cement or concrete after application, but not mortar. This is the frequent origin of claims regarding the quality of the applied product. This has aroused interest among producers to acquire a better knowledge on the effect of temperature and soaking on the mortar curing process at its early stages.

The influence of temperature on the properties of cement pastes and cement based mortars has been the subject of several studies. Thus, the morphology of C—H crystals, porosity and the formation of hydration shells are known to be affected when cement is cured at elevated temperatures [2]. Moreover, an increased hydration temperature has been found to accelerate early hydration of anhydrous phases in cement [3,4]. The hydration products thus formed are macroporous, heterogeneously distributed, and their long term compressive strength reduced [5]. In heat-cured mortars, delayed ettringite formation is favored and expansions common [6,7]. As found in cement pastes, the microstructure of the hydration products is also affected [8,9].

The above-described characteristics were derived from specimens cured at controlled environmental humidity. Usually, the samples are submerged in water at a constant temperature over long periods when the ambient conditions for a mortar wall are completely different in a dry atmosphere. The absence of moisture and the rapid increase in the mortar temperature caused by sunlight significantly alter its physico-mechanical properties. How soaking affects early curing in outdoor mortar applied at temperatures above room level has never to date been studied, however.

This work was intended to shed some light on the effect of heat on the curing process of fresh mortar. In order to mimic the heat produced by sunlight, mortar samples and cement pastes where exposed to IR light in the laboratory at controlled temperatures over the 40–80 °C range. Following heating, some samples where additionally subjected to soaking for a short time. The mechanical and physico-chemical properties of the studied samples confirmed the suitability of soaked mortars for plastering outer walls at temperatures above room level.

2. Experimental

2.1. Sample preparation

The studied material consisted of plastering cement based mortars produced by CEMKOSA. Mortar samples were prepared from cement,

---

* Corresponding author. Tel.: +34 957 218620; fax: +34 957 218621.
E-mail address: luis-sanchez@uco.es (L. Sánchez).

0008-8846/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconres.2009.04.002

Table 1
Chemical composition of Portland cement BL I 52.5 N.

Component	%
SiO_2	21.50
Al_2O_3	4.00
Fe_2O_3	0.20
CaO	65.40
MgO	1.35
SO_3	3.60
K_2O	0.40
CaO free	1.50
Cl^-	0.006
P.F. (loss on ignition)	0.40
R.I. (insoluble residue)	0.14
Density (g/cm^3)	3.05
Specific surface (Blaine)	4300

Table 2
Heat-curing time and temperature conditions used to obtain the mortar and cement samples.

Sample	Radiation time (h)	Temperature (°C)	Soaking
Mortar			
M25	–	25	No
M25 S	–	25	Yes
M40	4	40	No
M40 S	4	40	Yes
M60	4	60	No
M60 S	4	60	Yes
M80	4	80	No
M80 S	4	80	Yes
Cement			
C25	–	25	No
C25 S	–	25	Yes
C40	4	40	No
C40 S	4	40	Yes
C60	4	60	No
C60 S	4	60	Yes
C80	4	80	No
C80 S	4	80	Yes

Whether each sample was soaked is stated.

calcite and dolomite in a 13.5: 9.5:77 weight proportion. The composition of the Portland cement BL I 52.5 R used in this research is shown in Table 1. Mortar samples were cast in 40×40×160 mm molds, using a cement/sand ratio of 1:6 and a water/cement ratio of 1.07, which produced normal consistency [UNE-EN 1015-3] and acceptable workability. The samples were subsequently heat-cured under IR radiation. To this end, they were placed under IR lamps, the heating temperature being controlled via a sensor attached to the sample surface. A uniform temperature throughout the sample area was obtained by using four square aligned lamps. The mortar samples were heated for 4 h, which is roughly the time of maximal sunlight impingement on an outdoor mortar wall, at temperatures over the 40—80 °C range. Then, the samples were demolded and cured at 20 °C at 65 ± 5% relative humidity (RH) for 28 days (Fig. 1a). Some samples were soaked by immersion in distilled water for 5 min after 24, 48 and 72 h of curing (Fig. 1b). This short soaking procedure was intended to simulate the recommended irrigation treatment for plastering mortars. The cement pastes used to prepare the mortars were subjected to same process and characterization analyses for comparison. Table 2 summarizes the curing conditions used for the cement pastes and mortars.

2.2. Test procedures

Compressive strength tests were performed in accordance with UNE-EN 1015-11 after 24 h and 28 days of curing. Pore size distribution was determined with a Micromeritics AutoPore IV 9500 mercury porosimeter after 28 days of curing. For these measurements, samples were placed in a desiccator coupled to a vacuum pump in order to remove moisture until weight constancy. Microstructural changes were examined with various techniques. Mid—Infrared spectra for the cement pastes were obtained on a Nicolet Magna 510 Fourier transform IR spectrometer (FTIR) equipped with a DTGS detector and a CsI beamsplitter. For each sample, 256 scans were recorded over the 4000– 400 cm^{-1} spectral range with a resolution of 4 cm^{-1}. Spectra were obtained by using dried KBr pellets 12 mm in diameter (0.15 mg of sample and 150 mg of KBr). Thermogravimetric analysis (TG) was done with a Setaram “Setsys Evolution 16/18” thermobalance, heating from 25 to 850 °C at a rate of 5 °C min^{-1}. Crystal phases were identified by X-ray diffraction (XRD) on a Siemens D5000 apparatus using Cu Kα radiation and silicon as reference.

3. Results and discussion

3.1. Influence of temperature and soaking

Fig. 2a illustrates the influence of the heating temperature on the compressive strength of unsoaked mortars cured for 24 h. All measurements were made in quintuplicate in order to ensure reliability in the results of the mechanical tests. For comparison, cement pastes subjected to identical experimental conditions were also studied (see Table 2).

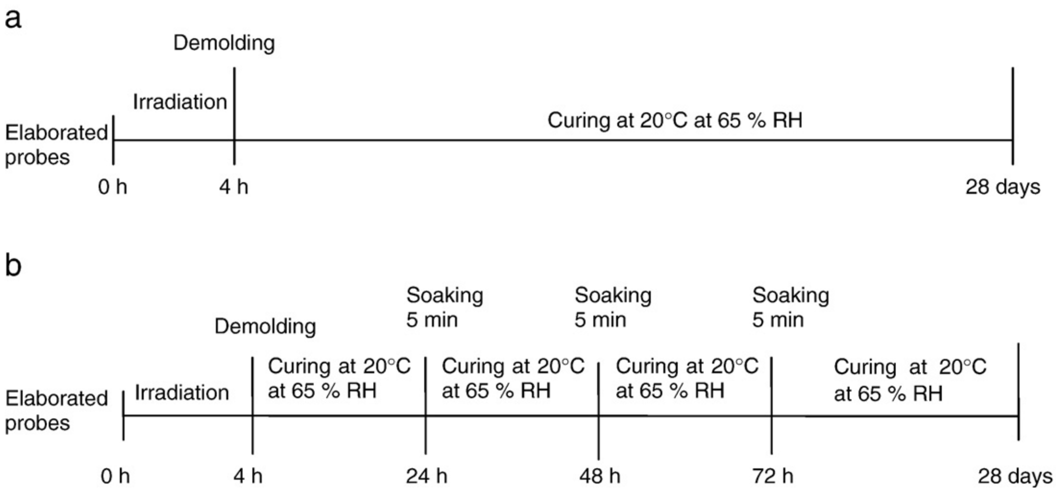

Fig. 1. Preparation procedures for (a) unsoaked and (b) soaked samples.

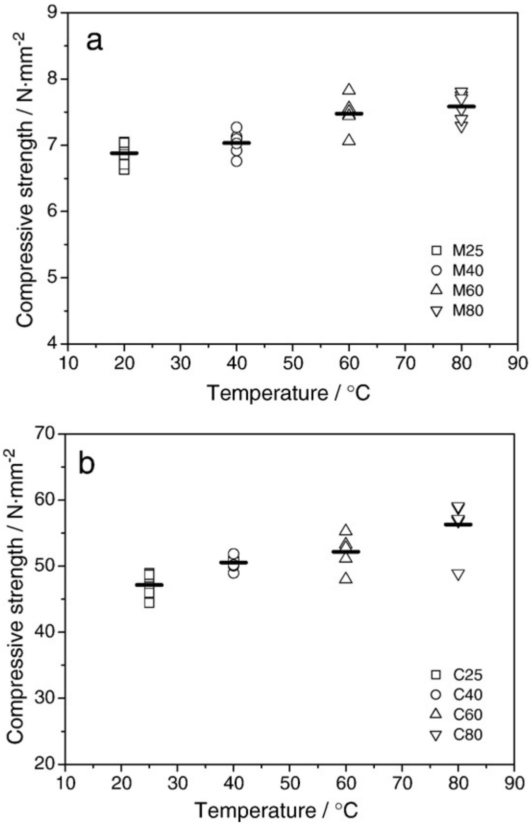

Fig. 2. Compressive strength as a function of the heat-curing temperature in 24 h old mortar (a) and cement samples (b).

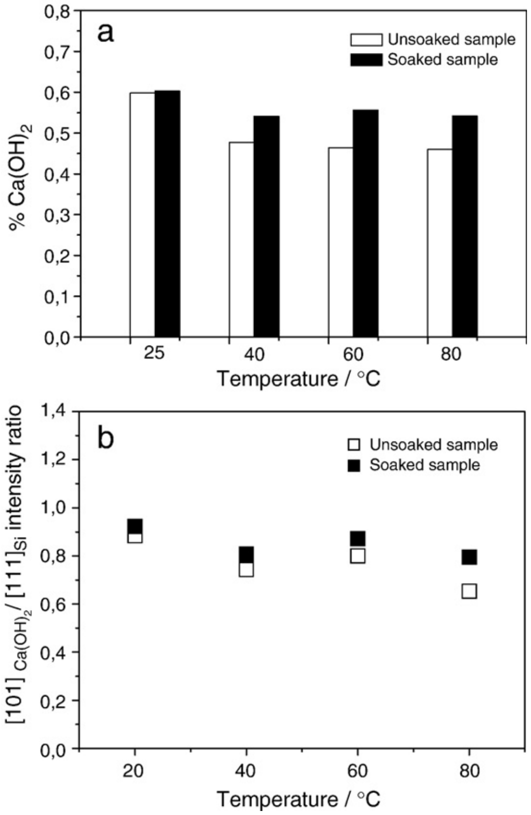

Fig. 3. Amount of portlandite estimated from TG analysis (a) and from (101)/(111) Ca(OH)$_2$/Si intensity ratio (b) for unsoaked/soaked mortar samples heated at different temperatures. Samples were cured for 72 h.

Compressive strength in both types of samples increased with temperature to a similar extent (~10%, Fig. 2b), indicating an accelerated curing. Similar results were previously reported by Lothenbach et al., who found dissolution of anhydrous clinker phases to be accelerated by increasing the temperature in Portland cement pastes [5]. Also, they found hydration products to form faster, and portlandite (C-H), C–S–H and ettringite to precipitate after 3 h of hydration at 50 °C.

Although an increased temperature favours the formation of hydration products, the soaking procedure was that dictating the evolution of the curing process. Fig. 3a shows the amounts of C-H formed, as estimated from the step between 425 and 450 °C in the TG curves for samples cured for 72 h using procedures described in Fig. 1. As can be seen, the amount of C-H was significantly smaller in unsoaked samples and more similar among soaked samples. Unexpectedly, the amount of C-H is reducing as temperature increases. Therefore, the significant release of water from mortar — necessary to obtain hydrated products — during heating hinders its curing. However, curing in heated mortar can be virtually completely restored by soaking. This was confirmed by XRD measurements. Fig. 3b shows the relative intensity of the [101] C-H diffraction line for all samples against Si as reference. Crystallization of the C-H phase was more marked in all soaked samples.

Significant differences in strength changes with temperature were found after 28 d of curing, particularly in the unsoaked mortar samples (Fig. 4a). Thus, such samples exhibited a dramatic decrease in compressive strength with increasing heating temperature, which facilitated their mechanical degradation. This adverse effect disappeared if the mortars were subjected to successive soaking for short times. In fact, the compressive strength returned to values similar to those for the samples cured at room temperature (see Fig. 4a). Therefore, soaking applied to fresh mortar is effective toward maintaining optimal mechanical properties over long curing times at elevated temperatures.

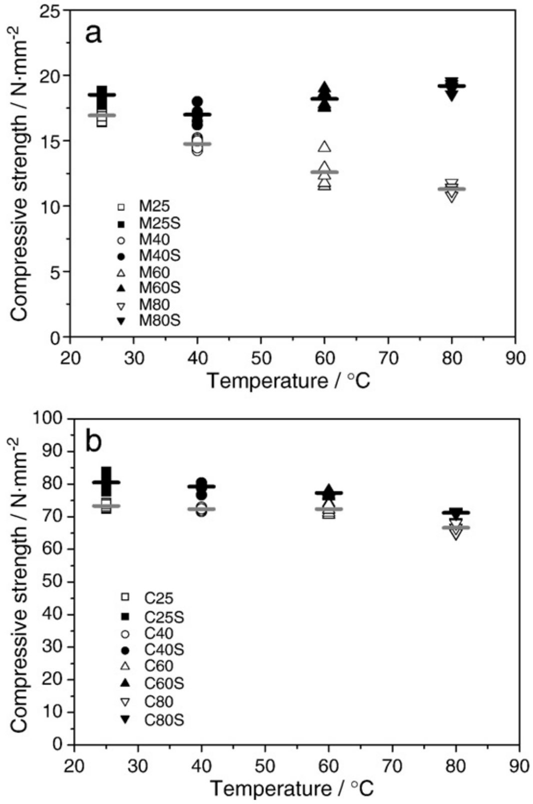

Fig. 4. Compressive strength as a function of heating temperature; (a) mortar and (b) cement specimens cured for 28 d. Black and white symbols correspond to soaked and unsoaked samples, respectively.

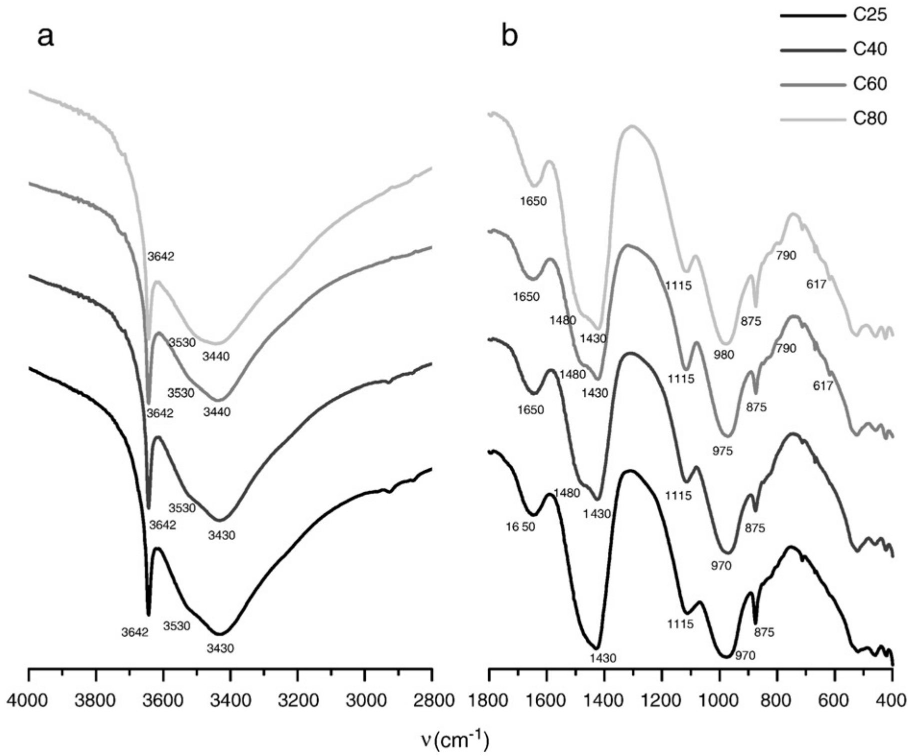

Fig. 5. Mid-IR spectra for unsoaked cured cement pastes (undried KBr pellets): (a) OH stretching region, (b) silicate and carbonate environments.

In summary, the increased temperatures caused by IR irradiation increase the strength of 24 h cured mortars, but decrease that of 28 d cured mortars. Soaking in water is a simple remedy to restore mortar strength.

Conversely, the curing temperature had little influence on the cement pastes (Fig. 4b). Thus, soaked pastes exhibited higher strength values, and a small decrease in strength was observed on increasing temperature of both types of samples. These results contrast with those reported by Escalante-García et al. [3], who found neat cement cured at relatively high temperatures (40–60 °C) to exhibit degraded mechanical properties at 28 and 360 days of curing. Thus, compressive strength was found to decrease by only 4% in our tests relative to 30% found by Escalante-García in neat cement samples also cured at 60 °C. Although increasing the temperature accelerated the hydration of anhydrous phases, hydration in the longer term was less marked in the pastes cured at the highest temperatures. The formation of a hydration shell around cement grains [2,3,8,10] at the beginning of curing directs hydration reactions to the inside of particles. Thus, products cured at different temperatures exhibited different microporosity and hence a different compressive strength. The difference between our results and those of Escalante-García et al. [3] may have arisen from differences in the heating conditions. Thus, these authors used a constant temperature throughout the curing process. Prolonged exposure to a high curing temperature has a strong effect on hydration and can lead to varying results.

3.2. IR analysis

As recently found, FT-IR spectroscopy is very useful for delineating the complex chemistry of cement, a result of the poor crystallinity of silicate hydrates [11–13]. Here, the hydration process was monitored by using this technique in order to obtain a better knowledge of the hydration products formed. Fig. 5 shows the mid-IR spectra for unsoaked cement pastes, and Fig. 5a the OH stretching region for the mixtures. Interpretation of the OH stretching region in mid-IR spectra (~2800–3750 cm^{-1}) is difficult because bands are broad. The lower frequency values, ν_w (3430 cm^{-1}), characterize the stretches of the molecular water OH-groups involved in strong hydrogen bonds with adjacent water molecules [14]. The high frequency stretch, ν'_w (3530 cm^{-1}), which appears as a shoulder, can be assigned to the water OH-groups directed towards the surfaces, which form weak hydrogen bonds with other water OH-groups. There is a graded variation in the IR transmittance for the –OH characteristic peaks with temperature. The lower curing temperature is, the higher is the $T\nu_w/T\nu'_w$ ratio (Table 3). The difference can be ascribed to differences in –OH location. Raising the temperature increases the amount of bonded OH species adsorbed on surfaces and decreases the $T\nu_w/T\nu'_w$ ratio as a result. The increase in OH surface — adsorbed species is related with the development of C–S–H silicate chains. The band at 3640 cm^{-1} is due to Ca–OH vibrations in portlandite.

Fig. 5b shows the spectra for dry cured cement pastes in the lower frequencies; this range provides useful information about silicates (C–S–H polymerization) and carbonates. In hydrated Portland cements, the main mid-IR bands for C–S–H gels appear at ~970 cm^{-1} (Si–O stretching vibrations of Q^2 tetrahedra), 660–670 cm^{-1} (Si–O–Si bending vibration, which is influenced by the Si–O–Si angle and occupancy of neighboring sites), and 450–500 cm^{-1} [11]. These mid-IR bands change systematically in frequency and/or intensity with the Ca/Si ratio in C–S–H, which is also related with silicate polymerization. The band at 970 cm^{-1} is assigned to Si–O stretching vibrations in C–S–H gels with a jennite type structure. The slight shift in the 970 cm^{-1} band to a frequency of ~980 cm^{-1} in the sample cured at 80 °C can be ascribed to

Table 3
IR transmittance ratios for the –OH characteristic peaks (3430 and 3450 cm^{-1}), in soaked and unsoaked cement pastes.

Sample	$T\nu_w/T\nu'_w$ unsoaked	$T\nu_w/T\nu'_w$ soaked
C25	0.88	1.18
C40	0.90	0.90
C60	0.90	0.89
C80	0.73	0.82

slight polymerization in the C–S–H chain. According to Farmer [15], T–O stretching vibrations in tetrahedral TO_4 groups (T=Si or Al) lie at 760–900 cm^{-1}. The band at 790 cm^{-1} for the samples cured at 60 and 80 °C, which can be assigned to stretching vibrations in O–Si–O groups, is also assigned to polymerization of C-S-H chains. Ettringite bands typically appear at 1100 and 610 cm^{-1} [14]. In Fig. 5b, ettringite bands appear at ~1115 cm^{-1} and 617 cm^{-1}. The absorption peaks at 1430 and 875 cm^{-1} indicate the presence of calcite as the main carbonate polymorph; however the absorption peak appearing at 1480 cm^{-1} when the temperature is raised suggests the additional presence of vaterite [16].

The mid-IR spectra for soaked cement pastes are shown in Fig. 6. These samples exhibited very similar infrared spectra, which suggest that the microstructure of cement pastes evolves in the same manner. The curing temperature affects the kinetics of hydration reactions; however, brief soaking seems to have no significant influence on the final structure of cement pastes, as the similarity between the infrared spectra suggests. The structural information thus obtained is consistent with the observed compressive strength values.

3.3. Microstructure

From the previous results we can conclude that curing above room temperature for a short time and soaking influence the initial stage of curing in mortar, but not in cement paste. Differences in internal microstructure are probably behind the differences in the way mechanical properties change in the two. Pore structure is a useful property with a view to correlating changes in microstructure with curing and the resulting mechanical properties. Fig. 7 shows the cumulative and incremental pore volume as a function of pore diameter in 28 d cured mortar and cement paste samples. The pore diameters shown are consistent with reported values for mortar and cement [17,18], the mortar exhibiting a more open structure. No significant differences in this respect between soaked and unsoaked cement paste samples were observed, whatever the heating temperature, (Fig. 7a). On the other hand, the heating temperature influenced pore size in the mortar samples. Thus, the cumulative pore volume for the unsoaked mortars increased with increasing temperature (Fig. 7b) and significant changes were observed in the differential curve (Fig. 7c). Thus, a major peak was observed over the 0.3–3 µm range where the intrusion volume was much higher in the heated samples (especially in M60 and M80); this suggests the presence of a more porous structure. The differences exhibited by the heated samples are consistent with the degradation in their mechanical properties (Fig. 4a). Soaking mortars in water facilitates their curing and reduces the influence of temperature on pore volume. The cumulative pore volume was similar for all samples (Fig. 7d); however, the pore size distribution of the soaked samples was different (Fig. 7e). A comparison of unsoaked and soaked M25 and M80 samples revealed a slightly reduced amount of pores larger than 1 µm in addition to an increased amount of pores in the 0.03–0.4 µm range, both of which suggest that a finer microstructure was developing.

The observed internal microstructure of the mortar and cement samples is consistent with the corresponding measured strength values. The effect of temperature on microstructure can be explained in terms of the kinetics of hydration and the water evaporation process. At high temperatures, the hydration reaction is faster than is diffusion, so hydration products coat cement grains and leave a fairly open interstitial space [19]. This increases the number of coarse pores, as observed in samples M60 and M80, the effect being especially significant in mortar as a result of its opened structure favouring the release of water by evaporation. Also, the rapid crystallization of hydration products helps to close the smaller pores. One can therefore conclude that exposure to high temperatures has a detrimental effect on the microstructure of fresh mortar. Nevertheless, its coarse porosity allows it to retain large amounts of water during soaking, which facilitates subsequent reactivation of the curing process.

4. Conclusions

The effect of temperature on fresh mortar and cement pastes was evaluated. In order to mimic heating of outdoor building plastering by sunlight, samples were heated by exposure to IR light over short periods. The IR data confirmed faster formation of hydration products

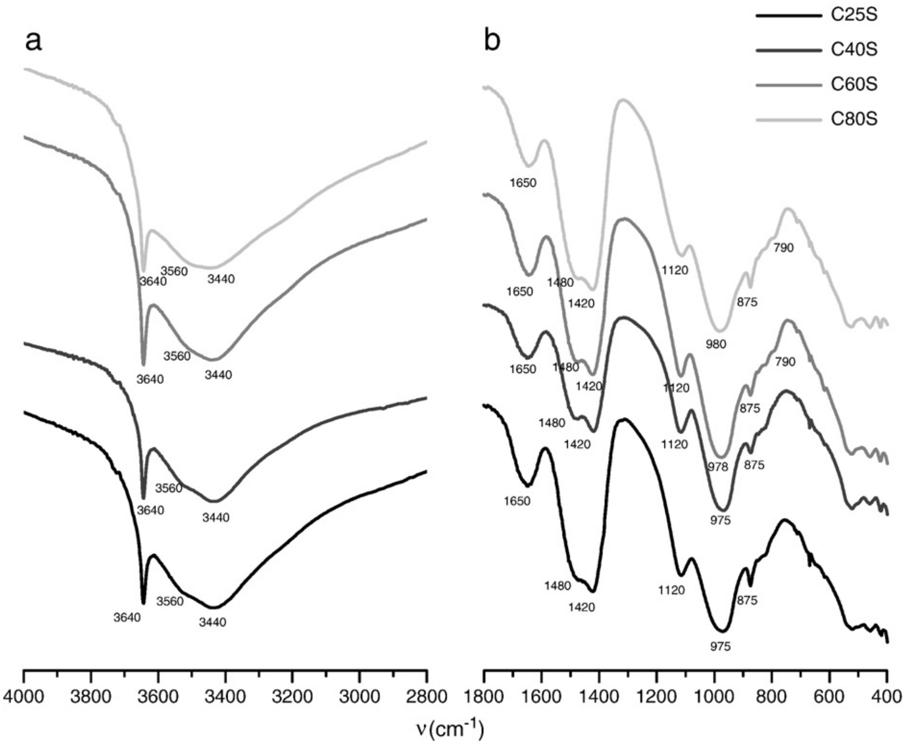

Fig. 6. Mid-IR spectra for soaked cured cement pastes (undried KBr pellets): (a) OH stretching region, (b) silicate and carbonate environments.

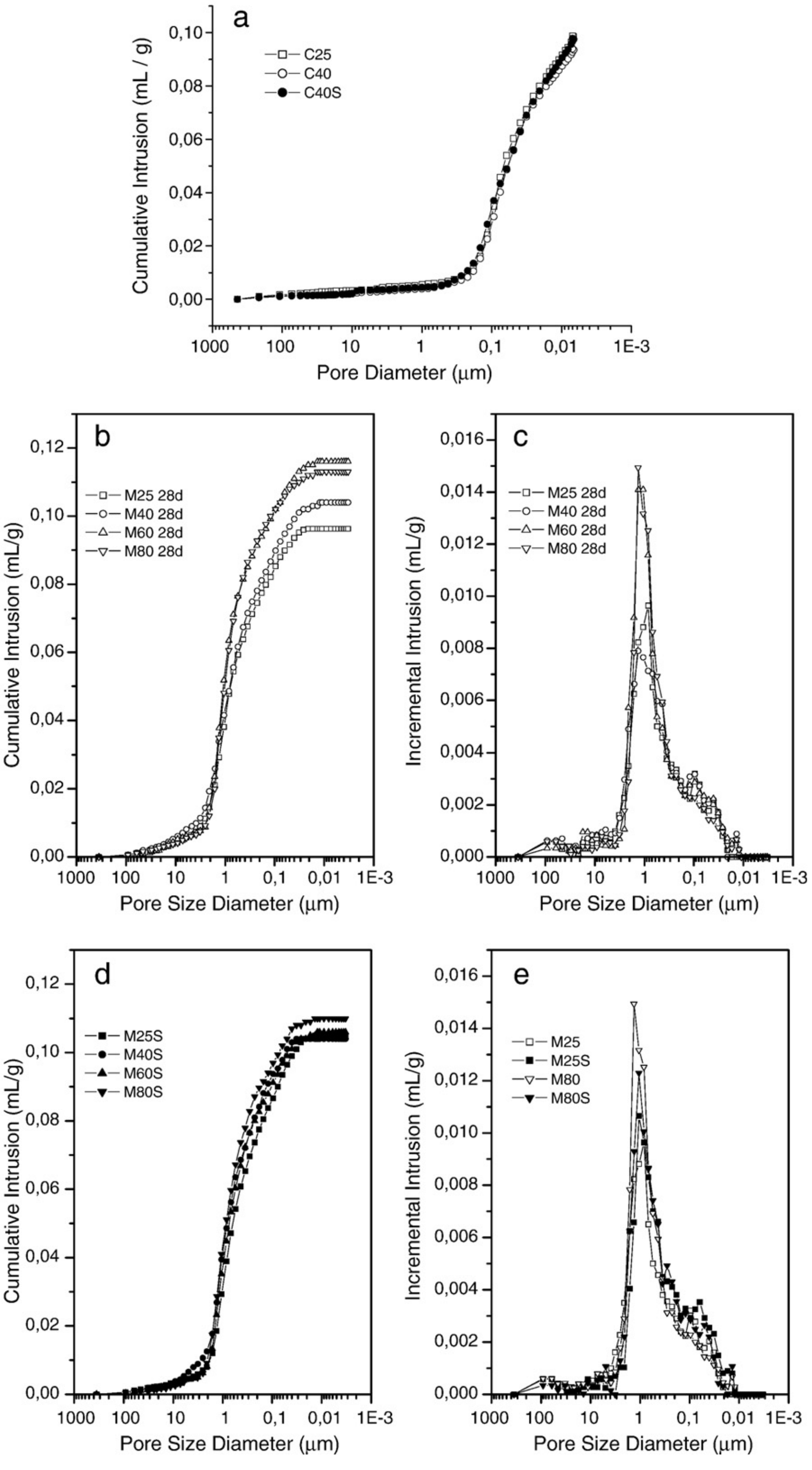

Fig. 7. Cumulative and incremental pore volume of cement (a) and mortar samples (b to e) subjected to varying curing temperature and soaking conditions.

with increasing temperature. Also, a deleterious effect on mechanical properties was observed. Early curing in neat cement cured under the specific conditions used here is barely affected by the temperature. On the other hand, exposure to high temperatures causes dramatic microstructure changes in mortar. These changes can be understood by considering two opposite effects: i) accelerated hydration which increases the compressive strength values at short curing periods (24 h) and ii) accelerated drying that hinders the curing process (lower C-H formation and developed strength values at 28 d). Nevertheless, successive soaking over short periods helps reactivate the mechanism of curing and restore the expected mechanical properties. Thus, although manufacturers recommend applying outdoor building plastering at the earliest hours of day in summer [20], applying cement based mortar at high temperatures is also effective provided the specific curing process described here is performed later. This finding serves to clarify the way cement based mortars can be used in extremely hot weather.

Acknowledgements

This research was funded by Junta de Andalucía (Group FQM-175) and the firm CEMKOSA within the framework of Project “Caracterización Analítica, Morfológica y Estructural de Morteros de Construcción. Desarrollo de Productos Adecuados Destinados a la Construcción, Rehabilitación y Restauración de Edificios y Monumentos Históricos y Contemporáneos”.

References

[1] O. Rodríguez-Mora, I. Azkárate, P. Ballester, R. Coll, F. García de la Cruz, D. Masó, E. Navarrete, P. Palacios, E. Quesada, A. Tébar, Morteros Guía General, Asociación Nacional de Fabricantes de Mortero, Madrid, 2003.
[2] K.O. Kjellsen, R.J. Detwiller, O.E. Gjorv, Development of microstructures in plain cement pastes hydrated at different temperatures, Cem. Concr. Res. 21 (1991) 179–189.
[3] J.I. Escalante-García, J.H. Sharp, Effect of temperature on the hydration of the main clinker phases in Portland cements: Part I, neat cements, Cem. Concr. Res. 28 (1998) 1245–1257.
[4] R. Yang, J. Sharp, Hydration characteristics of Portland cement after heat curing: I, degree of hydration of the anhydrous cement phases, J. Am. Ceram. Soc. 84 (3) (2001) 608–614.
[5] B. Lothenbach, F. Winnefeld, C. Alder, E. Wieland, P. Lunk, Effect of temperature on the pore solution, miscrostructure and hydration products of Portland cement pastes, Cem. Concr. Res. 37 (2007) 483–491.
[6] R. Yang, C.D. Lawrence, C.J. Lynsdale, J.H. Sharp, Delayed ettringite formation in heat-cured Portland cement mortars, Cem. Concr. Res. 29 (1999) 17–25.
[7] R. Barbarulo, H. Peycelon, S. Prené, J. Marchand, Delayed ettringite formation symptoms on mortars induced by high temperature due to cement heat hydration or late thermal cycle, Cem. Concr. Res. 35 (2005) 125–131.
[8] C. Famy, K.L. Scrivener, A. Atkinson, A.R. Brough, Effects of an early or a late heat treatment on the microstructure and composition of inner C–S–H products of Portland cement mortars, Cem. Concr. Res. 32 (2002) 269–278.
[9] P. Ballester, I. Mármol, J. Morales, L. Sánchez, Use of limestone obtained from waste of the mussel cannery industry for the production of mortars, Cem. Concr. Res. 37 (2007) 559–564.
[10] K.L. Scrivener, The effects of heat treatment on inner product C–S–H, Cem. Concr. Res. 22 (1992) 1224–1226.
[11] P. Xu, R.J. Kirckpatrick, B. Poe, P.F. McMillan, X. Cong, Structure of calcium silicate hydrate (C–S–H): near-, mid-, and far- infrared spectroscopy, J. Am. Ceram. Soc. 82 (3) (1999) 742–748.
[12] A. Hidalgo, S. Petit, C. Domingo, C. Alonso, C. Andrade, Microstructural characterisation of leaching effects in cement pastes due to neutralisation of their alkaline nature. Part I: Portland cement pastes, Cem. Concr. Res. 37 (2007) 63–70.
[13] F. Farcas, Ph. Touzé, La spectrométrie infrarouge à transformée de Fourier (IRTF). Une méthode intéressante pour la caractérisation des ciments, Bulletin des laboratoires des Ponts et Chaussées 230 (2001) 77–88.
[14] A. Hidalgo, J.L. García-Calvo, J. García-Olmo, S. Petit, M.C. Alonso, Influence of silica fume and fly ash additions on calcium aluminate cement hydration. A spectroscopic study and scanning electron microscopic evaluation, J. Am. Ceram. Soc. 91 (4) (2008) 1258–1265.
[15] V.C. Farmer, The Infrared Spectra of Minerals, Mineralogical Society, London, 1974.
[16] A. Hidalgo, C. Domingo, C. García, S. Petit, C. Alonso, C. Andrade, Microstructural changes induced in Portland cement-based materials due to natural and supercritical carbonation, J. Mat. Sci. 43 (2008) 3101–3111.
[17] J. Lanas, J.I. Alvarez, Masonry repair lime-based mortars: factors affecting the mechanical behaviour, Cem. Concr. Res. 33 (2003) 1867–1876.
[18] R.A. Cook, K.C. Hover, Mercury porosimetry of hardened cement pastes, Cem. Concr. Res. 29 (1999) 933–943.
[19] A.A. Almsallam, Effect of environmental conditions on the properties of fresh and hardened concrete, Cem. Concr. Compos. 23 (2001) 353–361.
[20] Internal communication from Grupo PUMA producer; www.grupopuma.com.