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Short communication

Halting the calcium aluminate cement hydration process

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Abstract

Calcium aluminate cement reactions with water result in anhydrous phases dissolution, followed by nucleation and crystal growth of hydrate compounds. Due to the dynamic characteristics of this process and in order to evaluate the phase transformation kinetics of such materials, suitable methods to halt hydration are required. In this work, the use of acetone and microwave drying, aiming to withdraw free water and inhibit further reactions, was evaluated. X ray diffraction was used to quantify the phases generated in the cement samples kept at 37 °C for 1–15 days. The advantages and drawbacks of these procedures are presented and discussed. Using microwaves to halt the hydration process in shaped samples seems to be effective to withdraw the cement free water, if a previous grinding of the material is carried out. The procedure suggested can be used in researches in the refractory castable area, endodontic cements and others.

Keywords: Calcium aluminate cement (CAC); Hydration; Microwave

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1. Introduction

Although calcium aluminate cement (CAC) hydration is an issue of great importance both in the industrial and commercial aspects, the chemical transformations involved in this process are still not well understood due to their complexity. CAC reaction with water usually leads to the generation of various phases known as hydrates, such as: $Ca_3Al_2O_6{\cdot}6H_2O$ (C_3AH_6), $Al_2O_3{\cdot}3H_2O$ (AH_3), and the metastable compounds $CaAl_2O_4{\cdot}10H_2O$ (CAH_{10}), $Ca_2Al_2O_5{\cdot}8H_2O$ (C_2AH_8), $Ca_4Al_2O_7{\cdot}xH_2O$ ($x = 7$, 11, 13 and 19) and AH_3 gel. The type and amount of the resulting hydrate phases depend on the mineralogical composition of the cement material, water/cement ratio used to prepare the pastes, curing time and mainly the temperature [1–4].

However, in order to analyze the cement paste composition at particular time intervals, it is necessary to halt the hydration process, withdrawing the free water in the material. This is a current concern as the sample preparation for further analysis may take hours or days, while the cement keeps hydrating and changing its phase composition [5].

Various methods are used to withdraw the free water (also known as capillary water [6]). Some of them involve drying (using an oven, or vacuum, etc.), whereas others are based on replacing water with a low surface tension organic liquid (such as acetone, ethanol, ether, methanol or isopropanol) [5,6]. Despite this, using solvents has been criticized by various authors [7–9] due to their possible interaction with some cement hydrates, this method is still commonly used before thermal analysis and other experimental techniques applied for the Portland and calcium aluminate cement investigations.

On the other hand, recently the use of microwaves (a high frequency electromagnetic radiation having a wavelength in the 1 mm to 1 m range [10,11]) has been applied to determine the water/cement ratio of concrete compositions [12] and to investigate the hydration of Portland cements [13]. Thus, there is still a lack of research concerning the use of this method for calcium aluminate cement.

Aiming to understand and study the phase transformations of a commercial CAC (Secar 71) during the curing process, this work evaluates the use of acetone or microwave drying in order to halt hydration. The collected samples were analyzed by X ray diffraction (XRD) and thermogravimetry (TG) techniques and a comparison between these procedures pointing out the advantages and drawbacks of each method is discussed.

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Table 1
Chemical composition of Secar 71 analyzed.

Chemical composition	Amount (wt%)
$CaAl_2O_4$ (or CA)	56.4
$CaAl_4O_7$ (or CA_2)	39.6
Al_2O_3	1.9
$Ca_{12}Al_{14}O_{33}$ (or $C_{12}A_7$)	2.1

2. Experimental

Secar 71 (Kerneos, France – Table 1) was chosen to be evaluated in this work and the cement pastes were prepared using a water/cement ratio (W/C) of 0.3, 0.4 or 0.5. Following the mixing step, cylindrical samples (diameter = 11 mm × height = 22 mm) were cast under vibration and kept in a moisture-saturated environment (~100% RH) for 20 h at 37 ± 1 °C (Nova Ética equipment, model 403/D). After that, the samples were demolded, immersed in distilled water and cured at 37 ± 1 °C. After a curing period of 1, 3, 7 and 15 days, some hydrated cement samples were subjected to microwave drying (Brastemp, model BMS25) for 6 min, using the highest power of this equipment (it can be observed that this condition allowed the fully free water withdrawal of the cement, resulting in a constant mass value). Besides that, some samples were also immersed in acetone (Labsynth, acetone PA) for 6 h and further dried at about 30 °C for another 6 h.

After these two halting hydration procedures, the collected samples were ground and analyzed by X ray diffraction (Bruker equipment, model D8 Focus, CuKα radiation [$\lambda = 1.5418$ Å] and nickel filter, using 40 mA, 40 mV and scanning step = 0.02). The Rietveld method (Topas 4.2 software, Bruker) was used to analyze the XRD results in order to evaluate the amount of the hydrate phases comprising the collected samples for the chosen curing periods. Nevertheless, due to the lack of information in the literature about the symmetry and structure of the CAH_{10} and C_2AH_8 phases (where C = CaO, A = Al_2O_3 and H = H_2O), a semi-quantitative evaluation of these hydrates (EVA software, Bruker) was carried out based on the calculation of the relative area of their more intense peaks.

TG evaluations were also carried out in NETZSCH STA 449 equipment, using a heating rate of 10 °C/min with a synthetic air (80% N_2–20% O_2) flow of 50 cm^3/min and using α-Al_2O_3 as a correction standard. The relative weight loss of the cement hydrate phases was estimated considering the TG results between the initial and final temperatures of the corresponding DTG peaks [14]. Additionally, the apparent porosity of the CAC samples (before halting the cement hydration) was measured by the Archimedes method (ASTM C380-00), using kerosene as the immersion liquid.

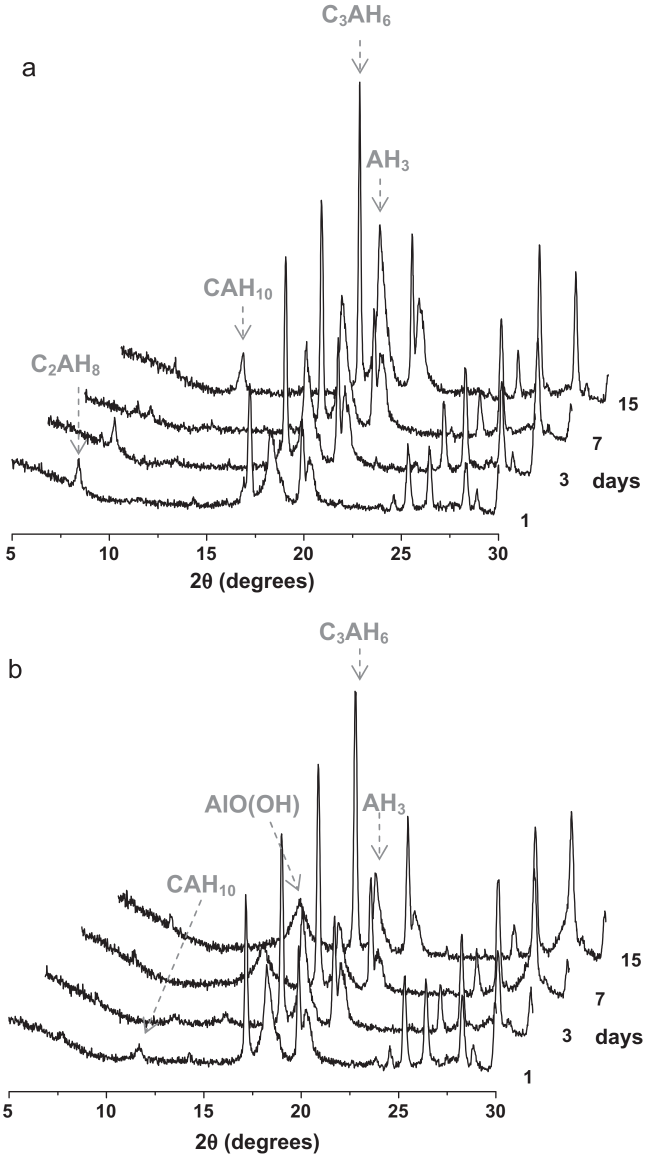

Fig. 2. XRD profiles for Secar 71 samples prepared with W/C = 0.3 (cured at 37 °C and immersed in distilled water) after halting the hydration with the use of (a) acetone and (b) microwave drying.

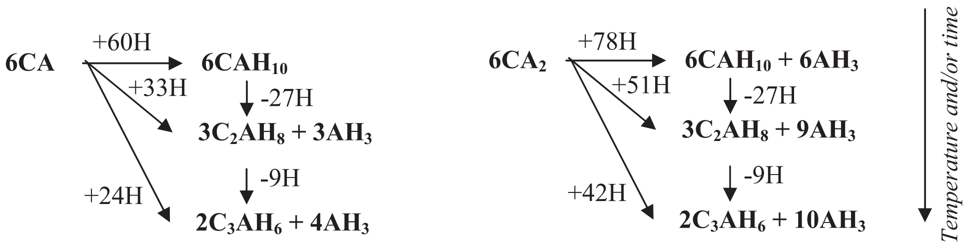

Fig. 1. General equations representing the hydrate generation reactions for the calcium aluminate cement [13].

3. Results and discussion

Secar 71 is mainly comprised by CA and CA_2 phases. The difference in the hydration process of theses anhydrous phases is related to the amount of Ca^{2+} and $Al(OH)_4^-$ ions which they can release in solution, defining which hydrate can be generated [15]. At 37 °C the precipitation of C_3AH_6 and AH_3 is induced, but because the cement samples evaluated in this work were immersed in water, other metastable compounds were still able to be formed due to the great liquid availability (Fig. 1).

According to the XRD results (qualitative – Fig. 2 and quantitative – Fig. 3), the main identified hydrates were C_3AH_6 and AH_3, but other phases such as CAH_{10}, C_2AH_8 and AlO(OH) (bohemite) were found in lower amounts. Moreover, this latter hydrate was only identified in the samples prepared with W/C = 0.3 (~5.6 wt% after 3 days) after microwave drying.

Some authors state that the bohemite formation is not usually identified along the CAC hydration under normal pressure conditions and its presence is favored when fast drying of the cement pastes provides a high internal pressure inside the humid material structure [16]. Thus, considering that the samples prepared with W/C = 0.3 presented the lowest porosity levels (Fig. 4), a suitable condition for increasing the local pressure inside the specimens might be attained during the microwave drying step, leading to AlO(OH) formation. After the drying procedure, some hydrated samples also presented cracks and this effect was associated to the water vapor release.

The presence of AlO(OH) in the microwave dried samples (W/C = 0.3) was followed by the decrease of $Al(OH)_3$ content and an expressive C_3AH_6 formation after 3 days of curing (Fig. 3). On the other hand, for the other evaluated conditions (W/C = 0.4 and 0.5, for both halting hydration procedures) the main observed transformations were the continuous increase of C_3AH_6 and $Al(OH)_3$ amounts as a function of time. These changes in the sample composition are related to the CA and CA_2 hydration and/or the conversion of the metastable hydrates (CAH_{10} and C_2AH_8), as shown in Fig. 1. Additionally, it must be highlighted that a significant amount of CAH_{10} and C_2AH_8 phases were identified when higher amounts of water were used during the cement paste preparation and, especially when the specimens were immersed in acetone to halt their hydration (i.e., $CAH_{10} = 2.3\%$-p for W/C = 0.5 after 7 days and $C_2AH_8 = 14\%$-p for W/C = 0.5 after 3 days – Fig. 3). The presence of these metastable hydrates in the Secar 71 samples might be an indicative that this organic solvent did not allow an

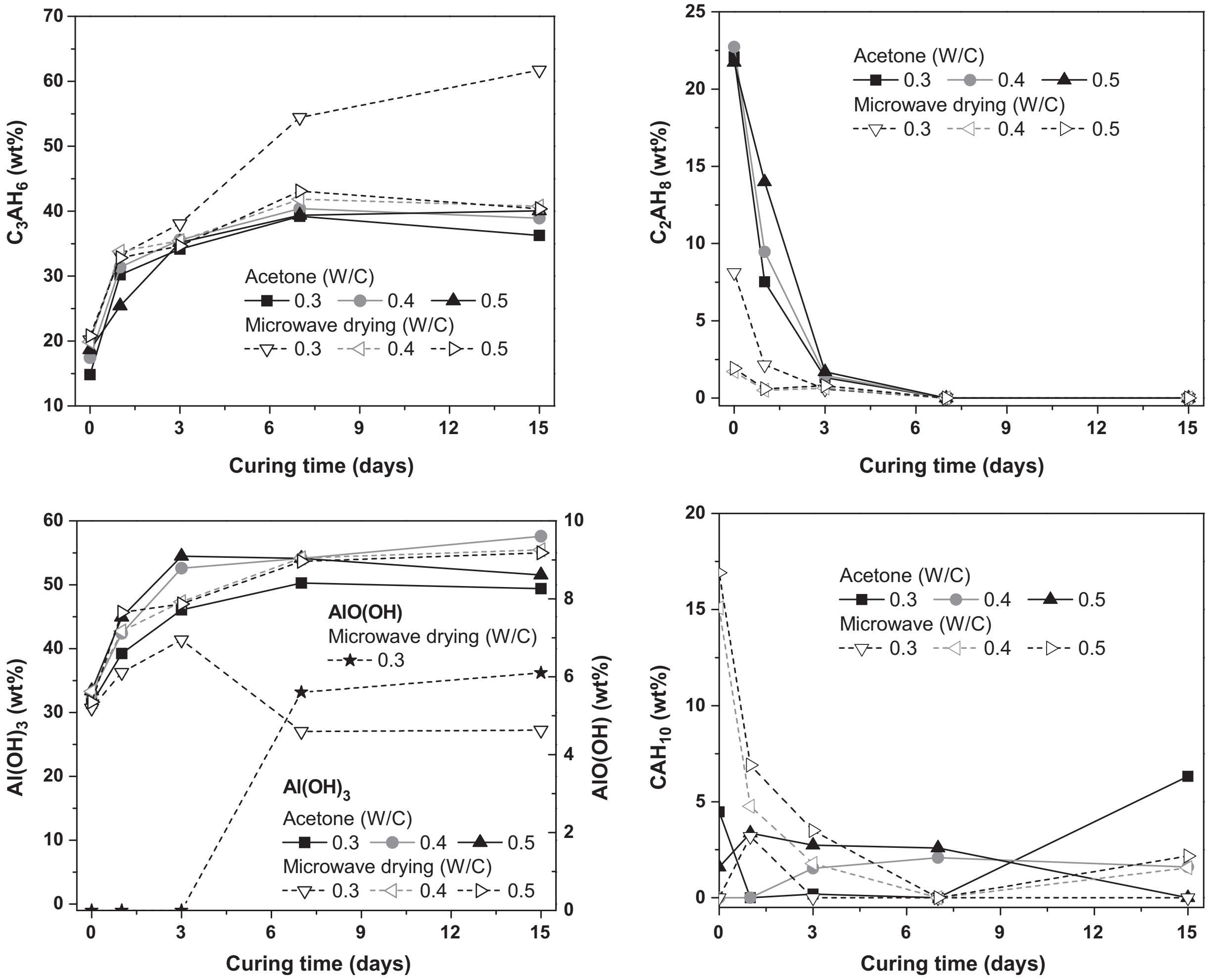

Fig. 3. Evolution of the hydrate phase contents for Secar 71 samples kept immersed in water at 37 °C.

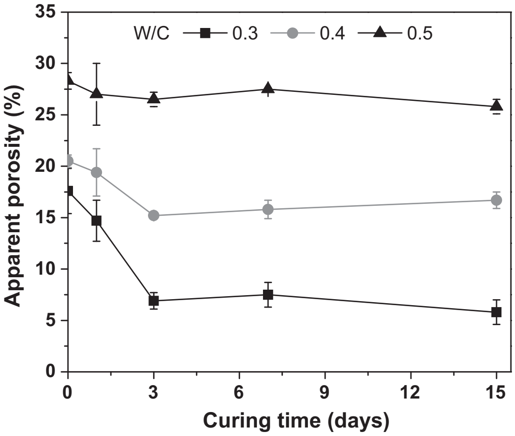

Fig. 4. Apparent porosity of the Secar 71 samples kept immersed in distilled water at 37 °C before drying.

efficient free water withdrawal, resulting in further reactions between this liquid and the cement anhydrous phases over time.

In order to better investigate the AlO(OH) formation and inhibit the high internal pressure inside the Secar 71 samples, avoiding the generation of phases which could change the sequence of transformations usually carried out in the hydration process, some cement specimens which were previously ground before the microwave drying step were also analyzed.

Table 2 presents comparative data among the main identified phases of the Secar 71 prepared with W/C = 0.3 and kept in water at 37 ± 1 °C for 15 days. These samples were hand ground (<90 μm) and placed in contact with acetone or microwave dried, following the same procedure described in the previous section.

Based on these data, it can be noticed that the AlO(OH) phase was not formed when the ground cement was dried in the microwave oven, which indicates that this hydroxide is only generated during the dehydration of the cylindrical samples. Thus, the grinding procedure of the cement before drying is required to provide a better evaluation of the CAC material. Moreover, the phase contents attained for both procedures (acetone or microwave drying) using ground samples are very similar (standard deviation lower than 4%) for all identified components (Table 2), which reinforces the fact that microwaves can be applied in the cement evaluation. Another important aspect is the more efficient free water withdrawal provided by the drying method, as observed in Fig. 5, confirmed by the lower dehydration peak at 88 °C (solid curve) and the lower weight loss attained by the TG and DTG analyses (Table 3, where the weight loss related to the free water content is presented in the column "H_2O lost from other hydrates", as other components such as AH_x gel can also be found in this temperature range). The cement samples immersed in acetone presented higher total weight loss than the dried ones for both tested conditions (after 1 and 15 days of curing, Table 3).

This trend was also observed by Saraya [11] and according to this work, the combined water contents of conventional

Table 2
Comparative data among the quantitative XRD results of the Secar 71 samples (W/C = 0.3) attained after 15 days of curing time.

Samples submitted to halt the hydration by	Phases (wt%)					
	CA	CA_2	CAH_{10}	C_3AH_6	AlO(OH)	$Al(OH)_3$
Acetone	2.6	4.6	6.3	36.3	0	49.4
Microwave	5.1	4.9	0	57.6	5.2	27.2
Acetone + grinding	1.8	2.7	2.9	36.7	0	54.9
Microwave + grinding	2.4	2.2	3.0	39.3	0	52.8

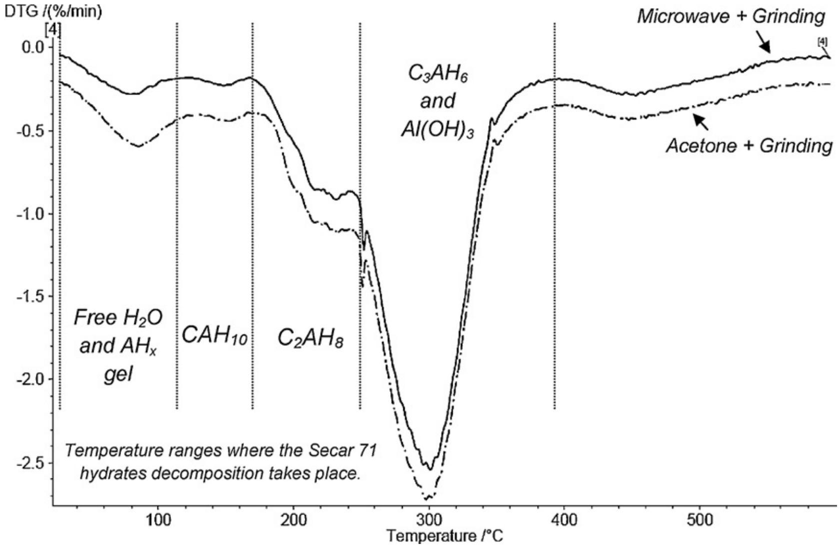

Fig. 5. DTG curves of Secar 71 samples prepared with W/C = 0.3 and kept in H_2O for 15 days at 37 °C (heating rate of 10 °C/min).

Table 3
Relative weight loss measured by TG and DTG of ground hydrated cement samples (W/C = 0.3) kept at 37 °C.

Halting hydration technique	Curing time (days)	H_2O from CAH_{10} (wt%)	H_2O from $Al(OH)_3 + C_3AH_6$ (wt%)	H_2O lost from other hydrates (wt%)	Total TG weight loss at 600 °C (wt%)
Acetone	1	1.3	17.3	6.2	24.8
	15	0.8	23.3	6.0	30.1
Microwave	1	1.1	18.5	6.0	23.4
	15	0.9	22.7	5.4	29.1

Portland and pozzolanic cement pastes attained after using acetone are higher than those for microwave drying. This is attributed to the fact that the organic solvents do not have the power to withdraw all the free water from the cement pastes, resulting in an increase of the combined water as a function of time due to further hydration reactions. On the other hand, Mohmel et al. [9] suggested that the higher degree of hydration of mono calcium aluminate samples washed with acetone/ether could be attributed to the surface changes of the unreacted CA and by a partial interaction (incorporation) of these solvents with the hydrates. Further evaluations are still required in order to investigate the microwave drying effect on the specific surface area and crystallinity of the Secar 71 cement samples.

Although the TG/DTG results (Table 3) could be used for a comparative analysis with the quantitative XRD data (Table 2), the overlap of some hydrate decomposition peaks inhibits an appropriate evaluation of such values. Nevertheless, according to the experimental results, the organic solvent seems to be less effective in halting the hydration reactions.

Therefore, a suitable water withdrawal (as attained by the microwave drying method) is required in order to avoid that, at longer times, the cement samples keep changing their compositions, resulting in inaccurate conclusions concerning the CAC transformations and properties.

4. Conclusions

C_3AH_6, $Al(OH)_3$, CAH_{10} and C_2AH_8 were the hydrated phases identified in Secar 71 shaped samples immersed in water and kept at 37 °C between 1 and 15 days. Although this temperature favors the formation of the stable phases (C_3AH_6, AH_3), the other metastable hydrates were also found, most likely, due to the continuous hydration of the anhydrous phases CA and CA_2 and the great water availability. Microwave drying of CAC samples seems to be a good alternative, when compared with the acetone one, to withdraw the free water and halt a further cement hydration. Nevertheless, it is strongly recommended that the cement material should be ground (before microwave drying) to inhibit some undesired effects, due to the increase of the internal pressure inside the humid sample induced by the fast drying of low porosity material, leading to some changes in the composition and formation of extra phases, such as AlO(OH).

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References

[1] F.A. Cardoso, D.M.M. Innocentini, M.M. Akiyoshi, V.C. Pandolfelli, Effect of curing time on the properties of CAC bonded refractory castables, J. Eur. Ceram. Soc. 24 (2003) 2073–2078.

[2] V.S. Ramachandran, Applications of Differential Thermal Analysis in Cement Chemistry, Chemical Publishing Company, New York, 1969, pp. 206–212.

[3] I.R. Oliveira, V.C. Pandolfelli, Castable matrix, additives and their role on hydraulic binder hydration, Ceram. Int. 35 (2009) 1453–1460.

[4] I.R. Oliveira, V.C. Pandolfelli, Does a tiny amount of dispersant make any change to refractory castable properties? Ceram. Int. 36 (2010) 79–85.

[5] N.C. Collier, J.H. Sharp, N.B. Milestone, J. Hill, I.H. Godfrey, The influence of water removal techniques on the composition and microstructure of hardened cement pastes, Cem. Concr. Res. 38 (2008) 737–744.

[6] E. Knapen, O. Cizer, K. Van Balen, D. Van Gemert, Effect of free water removal from early-age hydrated cement pastes on thermal analysis, Constr. Build. Mater. 23 (2009) 3431–3438.

[7] R.L. Day, Reactions between methanol and Portland cement paste, Cem. Concr. Res. 11 (1981) 341–349.

[8] H.F.W. Taylor, A.B. Turner, Reactions of tricalcium silicate paste with organic liquids, Cem. Concr. Res. 17 (1987) 613–623.

[9] S. Mohmel, W. Gessner, B. Kodderitzsch, A comparison of two different methods for stopping the hydration of mono calcium aluminate at 20 °C, in: Proceeding of International Cement Conference, Sweden, (1997), pp. 1–7.

[10] J. Cabrera, M.F. Rojas, Mechanism of hydration of the metakaolin–lime–water system, Cem. Concr. Res. 31 (2001) 177–182.

[11] M.E.I. Saraya, Stopping of cement hydration by various methods, HBRC J. 6 (2010) 1–8.

[12] T.R. Naik, B.W. Ramme, Determination of the water content of concrete by the microwave method, Cem. Concr. Res. 17 (1987) 927–938.

[13] M. Oriol, J. Pera, Pozzolanic activity of metakaolin under microwave treatment, Cem. Concr. Res. 25 (1995) 265–270.

[14] J. Dweck, P.M. Buchler, A.C.V. Coelho, F.K. Cartledge, Hydration of a Portland cement blended with calcium carbonate, Thermochim. Acta 346 (2000) 105–113.

[15] P. Pena, A.H. De Aza, Cementos de aluminatos cálcicos. Constitución, características y aplicaciones. In: Refractarios Monolíticos, Ed. Soc. Esp. Cerám. Y Vidrio, (1999) 85–106.

[16] C. Wohrmeyer, C. Parr, J.M. Auvray, M. Lievin, E. Frier, The impact of hydration and dehydration conditions on the permeability of LCC systems, in: Proceedings UNITECR 2007, 2007, pp. 1–8.