J Therm Anal Calorim (2010) 99:471–477
DOI 10.1007/s10973-009-0140-2

Study of alkaline hydrothermal activation of belite cements by thermal analysis

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Received: 13 February 2009 / Accepted: 26 May 2009 / Published online: 19 June 2009

Abstract The effect of alkaline hydrothermal activation of class-C fly ash belite cement was studied using thermal analysis (TG/DTG) by determining the increase in the combined water during a period of hydration of 180 days. The results were compared with those obtained for a belite cement hydrothermally activated in water. The two belite cements were fabricated via the hydrothermal-calcination route of class-C fly ash in 1 M NaOH solution (FABC-2-N) or demineralised water (FABC-2-W). From the results, the effect of the alkaline hydrothermal activation of belite cement (FABC-2-N) was clearly differentiated, mainly at early ages of hydration, for which the increase in the combined water was markedly higher than that of the belite cement that was hydrothermally activated in water. Important direct quantitative correlations were obtained among physicochemical parameters, such as the combined water, the BET surface area, the volume of nano-pores, and macro structural engineering properties such as the compressive mechanical strength.

Keywords Belite cements · Combined water · Thermal analysis · Mechanical strength

Introduction

Interest in belite cements began during the first energy crisis (years 70 of the last century). Recently, there has been renewed interest in these belite cements due to a second crisis that is taking place, caused by CO_2 emissions and their implications for climatic change. The Portland-cement manufacturing industry consumes more energy and produces more CO_2 emissions. As a result of concerns regarding global warming, pressure is being brought to bear on the cement industry to reduce CO_2 emissions.

Belite was named by Törneborn in 1897 to describe a crystal identified in a microscopic investigation of Portland cement [1]; the name is commonly used in the cement industry, but is not a recognised mineral name. Belite is a dicalcium silicate (Ca_2SiO_4) (C_2S) modified by incorporation of foreign ions and is normally present as the β polymorph (monoclinic symmetry), constitutes 15–30% of normal Portland clinkers. It reacts slowly with water contributing little to the strength during the first 28 days, but causes a substantial increase in strength at later ages [2].

Among the methods used for activating belite cements are those based on current cement technology: (i) the use of the most reactive low-temperature α'_L polymorph (orthorhombic symmetry), which is stabilised during clinker production by rapid quenching of the clinker and the introduction of impurity ions (alkalis, Fe, Al sulphate, and so on) into the crystal structure during formation [3–6], (ii) the use of low-temperature processes, which increase the surface area of C_2S and therefore its reactivity [7–23], and (iii) the addition of nano-materials during hydration [24–26].

The sol–gel process is a low-temperature process from which hydrated calcium silicates (mainly type C–S–H gel and/or hyllebrandite) with high-surface areas are obtained as precursors to belite cement. The precursors are then dehydrated by heating without grinding at temperatures ranging from 500 to 900 °C [7–9]; with this process, it is possible to achieve BET-N_2 surface areas between 7 and 13 $m^2\ g^{-1}$. Another low-temperature process is based on the formation of high-surface area precursors by hydrothermally treating the appropriate raw materials [10–26].

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Using the aforementioned procedure, we obtained belite cements (referred to as fly ash belite cement (FABC)), in which fly ash from coal combustion (class F [11–14] or class C [15–26]) was used as the raw material. The common technical characteristics of the cements are as follows: (i) the α'_L-Ca_2SiO_4 polymorph is as the main component, (ii) it contains elements, such as Fe, Al, Mg, Na and K, that increase its reactivity, (iii) it does not need to be ground, (iv) it can be used directly as cement without additional $CaSO_4$, since this is contained in the fly ash, and (v) it has excellent durability against the very concentrated salts that accompany low level radioactive waste (LLW) [14, 19–22].

Another possible process for activating belite cements is alkaline hydrothermal treatment of fly ash; in such a process, dissolution of fly ash is favoured, mainly the Al-compounds. Thus, the unit formula compositions, calculated as Ca_2SiO_4, for cements obtained from hydrothermal activation in water (FABC-2-W) or in alkaline NaOH solution (FABC-2-N) were as follows:

FABC-2-W: $Ca_{1.586}\ Mg_{0.016}\ Na_{0.011}\ K_{0.089}\ Si_{0.978}\ Al_{0.183}\ Fe_{0.024}\ S_{0.027}\ O_4$
FABC-2-N: $Ca_{1.528}\ Mg_{0.012}\ Na_{0.285}\ K_{0.048}\ Si_{0.816}\ Al_{0.357}\ Fe_{0.027}\ S_{0.028}\ O_4$

As can be seen, the belite phase is not pure, as it contains considerable amounts of other elements from the fly ash, including Al, Fe, S, Mg, Na and K. In the case of FABC-2-N cement, the Al content is higher than that of FABC-2-W and the Si content is lower. The difference indicates almost a 1:1 molar substitution of Si^{4+} by Al^{3+}, where the charge difference seems to be balanced by Na^+, whose content is 26 times higher than that in FABC-2-W. This excess of Na causes a decrease in the rest of the alkaline elements, K, Mg and Ca [17].

Thermal analysis is a useful tool for evaluating the pozzolanic activity of waste additions to Portland clinker [27–30] and for evaluating the effect of alkaline hydrothermal activation of fly ash belite cement, which is the main aim of this work.

The study was carried out by monitoring the increase in the combined water content over a 180-day hydration period. The results were compared with those obtained for a belite cement that was hydrothermally activated in water. The two belite cements were fabricated via the hydrothermal-calcination route of class-C fly ash in a 1 M NaOH solution (FABC-2-N) and demineralised water (FABC-2-W), according to the method described in previous works [17, 23]. Important direct quantitative correlations were obtained among physicochemical parameters, such as the combined water, the BET surface area, and the volume of nano-pores, and the macro structural engineering properties, such as the compressive mechanical strength.

Experimental

Materials

Raw materials

A mixture of class-C fly ash, from coal combustion (called FA-2), and commercial CaO with a Ca/Si molar ratio of 2, was used as raw material. The chemical composition of the starting fly ash, as measured by UNE 80-215-88 or EN 196-2, is listed in Table 1. The FA-2 was in accordance with the requirements of ASTM Class C and the EN-UNE 450 specifications ($SiO_2 + Al_2O_3 + Fe_2O_3$ contents lower than 70%, a high CaO content, and a CaO/SiO_2 molar ratio of 1). The crystalline phases, determined by X-ray powder diffraction (XRD), included free lime (CaO), anhydrite ($CaSO_4$), quartz (SiO_2), hematite (Fe_2O_3), magnetite (Fe_3O_4) and mullite (A_3S_2) ($Al_6Si_2O_{13}$).

The fly ash belite cements (FABC) were fabricated via the hydrothermal-calcination route. First, the cement precursors were obtained by hydrothermal treatment of the FA-2 in demineralised water (FABC-2-W) or in a 1 M NaOH solution (FABC-2-N). The belite cements were then obtained by heating the precursors at 800 °C. More details regarding characterization of the precursors and the fabrication process can be found in the literature [15, 17].

The chemical compositions of the cements are shown in Table 1. The crystalline phases were as follows: α'_L-C_2S (Ca_2SiO_4) polymorph with poor crystallinity, gehlenite (C_2AS) ($Ca_2Al_2SiO_7$), traces of mayenite ($C_{12}A_7$) ($Ca_{12}Al_{14}O_{33}$) and calcite (Cc) ($CaCO_3$). The main differences observed for the FABC-2-N cement were (i) a

Table 1 Chemical composition of the starting fly ash (FA-2) and anhydrous FABC-2-W and FABC-2-N cements (mass %)

	LOI[a]	CaO	SiO_2 (total)	Fe_2O_3 (total)	Al_2O_3	MgO	SO_3	Na_2O	K_2O	SiO_2[b] (reactive)	BET (m^2g^{-1})
FA-2	4.0	32.0	32.8	4.2	19.3	2.2	2.8	0.44	1.6	25.2	3
FABC-2 W	1.4	48.3	28.7	2.3	15.2	1.4	1.7	0.25	0.5	28.6	6.4
FABC-2-N	2.7	48.3	23.6	3.0	14.4	1.2	1.2	4.5	0.38	23.5	5.5

[a] LOI = Mass loss on ignition

[b] Silica reactive according to Spanish standard UNE-80-224

higher intensity and better definition of α'_L-C_2S (Ca_2SiO_4) XRD-peaks, and (ii) lower calcite and higher mayenite contents. The absence of free lime in the two cements suggested completed reactions. The calcite content (determined by thermogravimetric analysis) was 1.1% and 2.3% for FABC-2-W and FABC-2-N, respectively. It is interesting to note the high fineness of both cements (6.4 and 5.5 $m^2\ g^{-1}$ for FABC-2-W and FABC-2-N, respectively), obtained without grinding.

Sample preparation

Pastes were prepared at a demineralised water-to-cement ratio of 0.68 and 0.82 for FABC-2-W and FABC-2-N, respectively, containing 2% (by cement mass) of a commercial water reducer additive (Rheobuild-1000, Degussa Construction Chemicals, Barcelona, Spain). After mixing, a series of six prisms were moulded into 1 cm × 1 cm × 6 cm samples and compacted by vibration. The samples were demoulded after 1 day at >95% RH and cured at 20 °C under >95% RH in sealed containers for a period ranging from 1 to 180 days. The compressive mechanical strength was measured for each six-sample series. A portion of the samples were then cut into approximately 7 mm monolithic pieces. Nanoscale (1–100 nm) gel characterization was performed using the BET surface area and pore volume analysis. The monolithic pieces were first dried at room temperature in desiccators with silica gel, until a constant weight was recorded, to eliminate free water (evaporable water), and then about 0.5 g of sample was degasified at 50 °C (to prevent decomposition of C–S–H gel) under vacuum (up to 5 mm Hg).

Instrumentation

The hydrothermal treatment was carried out with a Parr (PARR Instrument Company, Illinois, USA) model 4522 (a 1,000 mL pump with a split-ring closure and a PID model 4842 temperature controller, Parr Instrument Co.). XRD patterns were recorded on a Philips (Eindhoven, the Netherlands) PW 1730 diffractometer with $CuK_{\alpha 1}$ radiation. Surface-area measurements were made by the BET multipoint method (Model ASAP 2010, Micromeritics Instrument Corp., Norcross, GA) using N_2—77 K gas. Surface areas were calculated from the sorption isotherm data using the BET method [31] in a relative pressure (P/Po) range of 0.003–0.3. Pore volumes were calculated according to the Barret–Joyner–Halenda method [32] using data from the adsorption isotherm branch. Thermal analyses were performed with a Netzsch STA 409 simultaneous analysis system (NETZSCH-Gerätebau GmbH, Selb, Germany) using 50 mg samples and a dynamic nitrogen stream (flow rate = 100 $cm^3\ min^{-1}$) at a heating rate of 10 $°C min^{-1}$. Before thermal analysis, the samples were dried at room temperature in desiccators with silica gel, to eliminate the evaporable water. The capillary porosity and pore-size distribution were investigated by mercury intrusion porosimetry carried out with a Micromeritics Pore Sizer IV 9600 V1.05, in a pressure range of 0.5-33000 psia.

Results and discussion

The rates of the hydration reactions of the two belite cements (FABC-2-W and FABC-2-N) were evaluated from the evolution of the combined water, measured by thermal analysis during 180 days.

The combined water, in cement chemistry terminology, is the total content of water molecules combined with solid hydrated compounds. In the case of the FABC cements, this originates from the following hydrated compounds: $C_2SH_{0.35}$ ($Ca_2SiO_4 \cdot 0.35H_2O$), C–S–H gel and calcium-monosulpho-aluminate (C_4AsH_{10}) ($[Ca_2Al(OH)_6H_2O]_2$-$SO_4 \cdot 5H_2O$) [17].

The TG and DTG profiles of the hydrated cements were similar to those shown in Fig. 1, which shows FABC-2-W and FABC-2-N cements after 180 days of hydration. A continuous mass loss between 25 and 700 °C is observed in

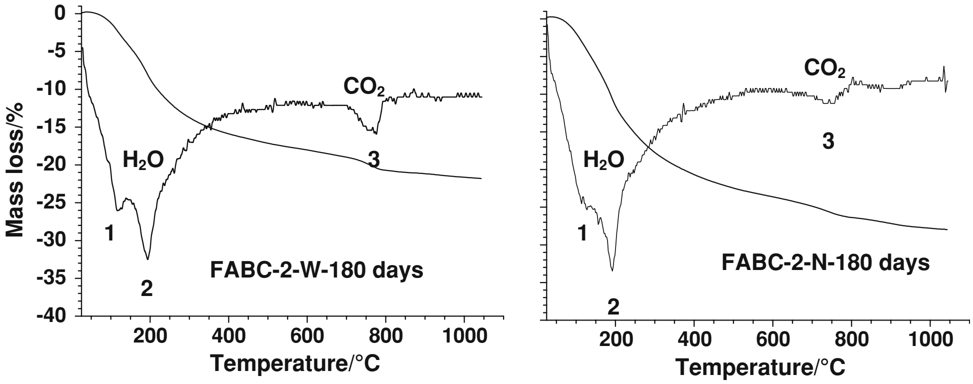

Fig. 1 TGA and DTG curves of FABC-2-W and FABC-2-N pastes hydrated for 180 days

the TG curves, which is due to the release of water from the hydrated products. In the corresponding DTG curves, two maxima are observed at 100 and 200 °C. A second mass loss is also observed between 700 and 1,100 °C, due to the release of CO_2 during calcite decomposition, which produces a DTG peak centred at 750–800 °C. Some of the $CaCO_3$ content was already present in the anhydrous FABC. This second mass loss was not considered for calculating the combined water.

The observed increase in combined water with hydration time, for the two belite cements, FABC-2-W and FABC-2-N, are shown in Fig. 2. Related physical and mechanical parameters, such as the surface area, the porosity of the C–S–H gel and the mechanical strength, have been reported in this figure for comparison [23].

As can be seen, the effect of the alkaline hydrothermal activation (FABC-2-N) is clearly accompanied by a rapid increase in the combined water at early ages of hydration, which practically stops after 28 days. The behaviour of FABC-2-W is more gradual and can be well described by a direct semi-logarithmic function. The difference diminishes at later hydration ages, at which the combined water was 23.0% and 26.5% for FABC-2-W and FABC-2-N, respectively.

The observed behaviour of surface area and mechanical strength with hydration time were similar to that of the combined water; the values for the hydrothermally activated alkaline cement (FABC-2-N) were markedly higher than those of the FABC-2-W, reaching a plateau after 28 days. At later ages (180 days), a slight decrease in surface area and mechanical strength was observed for FABC-2-N, whereas the values of the FABC-2-W were markedly lowers at early ages of hydration (up to 28 days) but were markedly higher than those of FABC-2-N at later ages.

The C–S–H gel significantly contributes to the observed increase in surface area upon hydration, due to its lower particle size compared with the other hydration products; therefore, one can hypothesize that the decrease in surface area and mechanical strength, observed at later ages for FABC-2-N, may be related to some change in the C–S–H gel.

Instability of the C–S–H composition with hydration time has been suggested by previous SEM/EDX characterization studies of FABC-2-N [17], in which a remarkable decrease in the Na/Ca atom ratio (from 0.11 to 0.022) was observed between 28 and 180 days of hydration. This can be explained if mobile, solvated Na ions $[Na(H_2O)_6]^+$ were located at the surface sites of the gel. Thus, it can be expected that a loss of solvated Na ions influences the distribution of the gel particles, likely compacting it and decreasing the porosity of the gel.

To verify this hypothesis, the nano-range (1–100 nm) porosity was measured by the N_2 adsorption isotherm method. These small pores are inherent to the particle packing of the C–S–H gel and are not detrimental to the mechanical strength; consequently, in the absence of other secondary phenomena, they must have a similar evolution, than that of combined water and surface area, with hydration time.

As can be seen in Fig. 2, this is true for FABC-2-W but not for FABC-2-N, where a decrease in the volume of gel pores resulted after 28 days (from 22% to 16.1%).

This decrease may be related to a change in the particle packing of the C–S–H gel, which causes a more compact gel, in which a loss in solvated Na ions plays an important role.

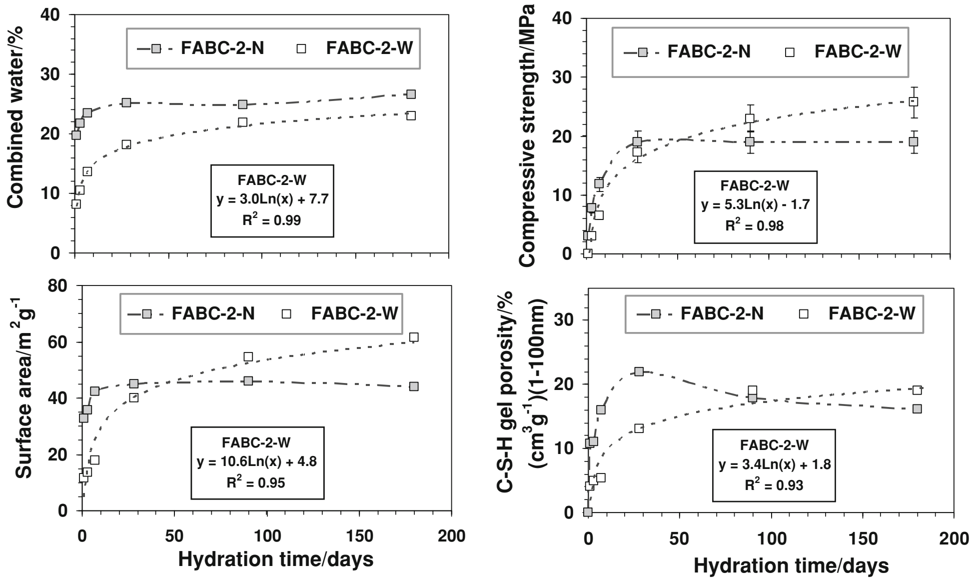

Fig. 2 Evolution of: combined water, compressive strength, surface area and porosity of C–S–H gel with hydration time. Influence of type of belite cement

The decrease in C–S–H porosity is accompanied by an increase in the amount of the capillary pores (>100 nm), as can be seen in Fig. 3 (from 4.8% to 7.7%), justifying the loss of mechanical strength observed in Fig. 2. The presence of larger capillary pores was also suggested by SEM (Fig. 4), in which compact C–S–H gel blocks of FABC-2-N that were hydrated for 180 days appeared together with micro cracks (capillary pores).

As a consequence of the increase of packing of C–S–H gel particles, the average pore diameter of the hydrothermally activated alkaline (FABC-2-N) C–S–H gel also decreased: from 24.9 to 15.4 nm between 28 and 180 days.

The connection between the loss of alkaline Na ions in the C–S–H and the decrease in the diameter of gel pores is presented in Fig. 5. The values corresponding to the C–S–H gel of hydrated FABC-2-W have been included for

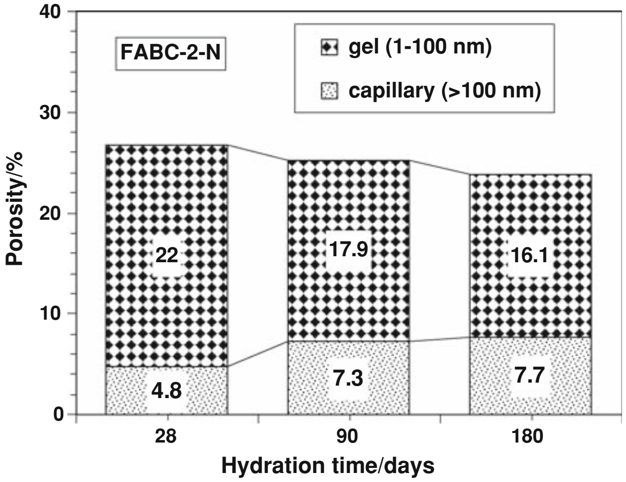

Fig. 3 Evolution of gel and capillary porosity of FABC-2-N hydrated cement calculated from N_2 adsorption isotherm (1–100 nm) and mercury intrusion porosimetry (>100 nm)

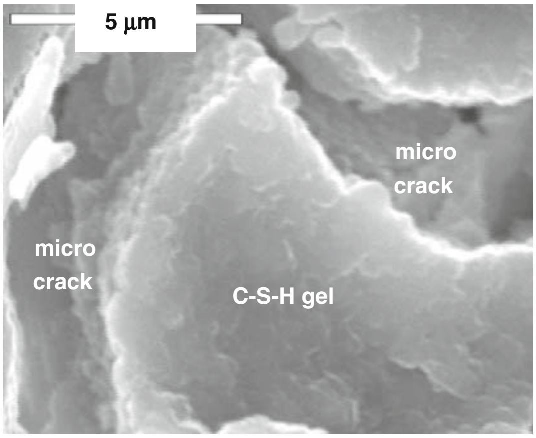

Fig. 4 SEM images of microcracks in C–S–H gel after 180 days of FABC-2-N hydration

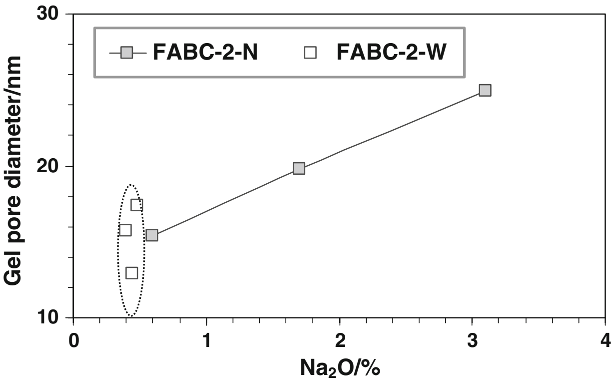

Fig. 5 Correlation of the percentage of Na (expressed as Na_2O) of the C–S–H gel and the average gel pore-diameter. Influence of type of belite cement

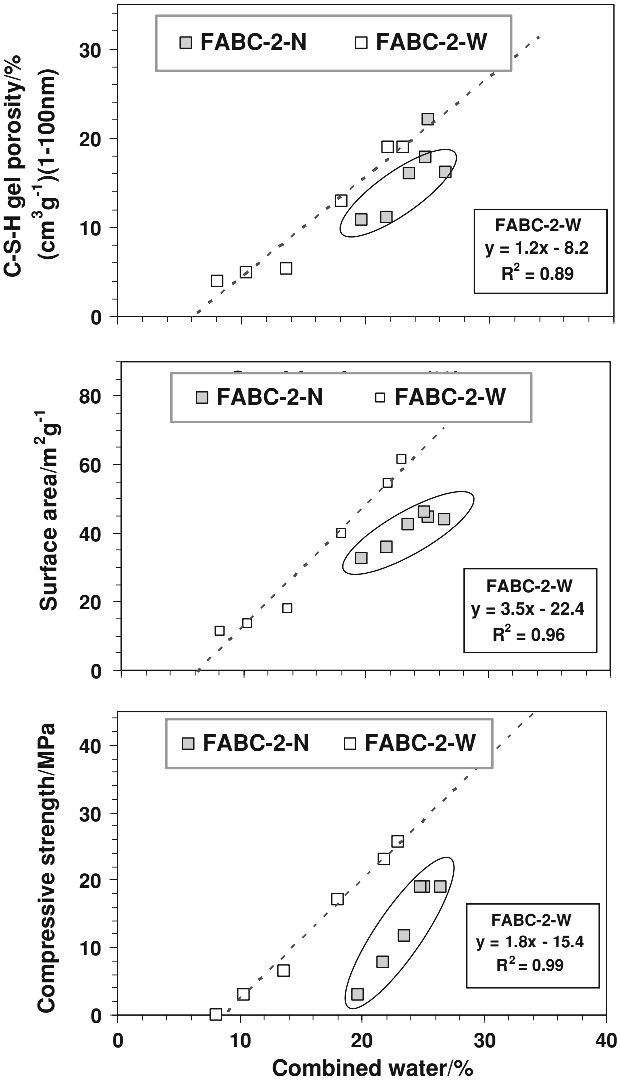

Fig. 6 Quantitative correlations among combined water and: compressive strength, surface area and porosity of C–S–H gel. Influence of type of belite cement

comparison. As can be seen, a direct linear correlation is established between the two parameters in the C–S–H gel of FABC-2-N; however, no correlation is observed for the values corresponding to the FABC-2-W cement.

Given the increased contribution of the C–S–H gel to the combined water, surface area and nano-porosity, which is responsible for the mechanical properties, quantitative correlations are expected between them, as can be seen in Fig. 6, in which direct linear regressions are obtained for FABC-2-W cement. In the case of FABC-2-N, the points are located, in general, to the right of the line, indicating higher combined water values compared with the FABC-2-W cement, perhaps due to the contribution of water molecules from the solvated sphere of sodium.

Conclusions

- Thermal analysis is a useful tool for quantitatively evaluating the effect of the alkaline hydrothermal activation of fly ash belite cement (FABC-2-N).
- This effect is manifested at early ages of hydration (up to 28 days) by a rapid increase in the combined water compared with that of FABC-2-W, which is accompanied by a concurrent evolution in compressive strength, surface area and porosity of the C–S–H gel.
- From 28 days of hydration, a densification of the C–S–H gel of the FABC-2-N cement is produced by the loss of mobile Na ions. This densification was accompanied by an increase in the size of capillary pores, perturbing the increase in the compressive strength, which decreased slightly.
- Important direct linear quantitative correlations were found between the combined water, determined by thermal analysis, and macro structural engineering properties, such as the compressive mechanical strength, for FABC-2-W. The correlations were not as distinct for FABC-2-N, likely due to other micro structural factors, such as the increase in the size of capillary pores (>100 nm) and the contribution of water molecules in the solvated Na sphere to the combined water.

Acknowledgements The authors gratefully acknowledge the financial support by the Minister of Science and Technology (Project n° MAT 2002-04023-CO3) and the Thermal Power Station of Cercs Catalonia, Spain for supplying the fly ash.

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