Modifications of the C-S-H gel by hydration at 40°C of belite cements from coal fly ash Class C

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Abstract

The influence of the temperature on two types of hydrated fly ash belite cement pastes were investigated at a nanoscale (1-100 nm) by measuring the specific surface area and pore-size distribution by the sorption isotherms of nitrogen gas and the BET method, and at a microscale from the pore-size distribution measured by mercury intrusion porosimetry. The two belite cements were fabricated by the hydrothermal-calcination route of fly ash class C in NaOH 1M solution (FABC-2-N) and demineralized water (FABC-2-W). In the case of FABC-2-W, a densification of the C-S-H gel was produced at the temperature of 40°C, which favored the formation of pores of ~3 nm of diameter leading to higher surface area values, compared with the C-S-H gel formed at 20°C. At a micro-scale, the temperature caused an increase of capillary porosity (>0.05 μm) at later age of hydration and, consequently, a decrease of compressive mechanical strength. In the case of FABC-2-N, the densification of the gel was less evident, but the increase of capillary porosity (pores of diameter >0.05 μm) was higher. Significant direct linear quantitative correlations were found among these nanostructure characteristics of the C–S–H gel and macrostructural engineering property such as the compressive mechanical strength, for the two FABC-2-W and FABC-2-N cements under normal conditions. At 40°C, the correlations were not so clear probably due to another microstructural factor such as the increase of the larger capillary porosity (>0.05μm).
Keywords: Temperature of hydration, BET-N$_2$ surface area and pore-size distribution, capillary porosity, C-S-H gel porosity, mechanical strength, fly ash belite cement.

I. Introduction

Fly ash belite cements (FABC) have different properties to those of Portland cement, which are of great importance for specific applications such as, the manufacture of cement-based-matrices for confining radioactive liquid wastes and for the dam construction, among others. FABC present a slow hydration rate, for what the heat that is liberated is more gradual, there being avoided shrinkage problems. The hydration of FABC produces minims amounts of Ca(OH)$_2$, and lower pH of pore-solution than that of Portland cement, circumstances that assuring a good durability in the aggressive atmospheres in which expansive reactions with Ca(OH)$_2$ could take place, as it is the case of the attack by sulphates, presents in great amount ie in the radioactive liquid wastes$^{1-6}$.

In this sense, we are investigating the use of FABC for the formulation of alternative matrices for confining low level liquid wastes (LLW) and medium level liquid wastes (MLW)$^{7-9}$. The storage of LLW and MLW in Spain is located in “The Cabril” near the city of Cordoba, where the temperature can reach values of 40ºC. For that, we are interested in studying the stability of FABC in that temperature, which is presented here.
In the case of Portland cement, there is a general consensus on the effect that the temperature causes on the microstructure, porosity and hydrated products. Skalny and Older\textsuperscript{10} studied from adsorption techniques the crystalline and near amorphous calcium silicate hydrates formed under different conditions from C\textsubscript{3}S, \(\beta\)-C\textsubscript{2}S and synthetic tobermorite. They observed that while the surface area continuously increases with the degree of hydration at 25°C, at higher temperatures, after reaching a maximum, the surface areas per unit of nonevaporable water, \(W_n\), decrease. The authors explained this as due to the existence of recrystallization processes, which could cause in coarsening of the hydration products. Paul and Glasser\textsuperscript{11} from the study on the impact of prolonged warm (85°C) moist cure on a commercial Portland cement paste, detected a very large increase in porosity at 85°C, which arises partly as a consequence of conversion of low-density paste constituents to higher density katoite. Cong and Kirkpatrick\textsuperscript{12} examined the structural changes in synthetic C-S-H with C/S ratio from 1.13 and 1.56 cured at relative humidities from 9\% to 100\% and temperatures from 25 to 200°C, using \(^{29}\text{Si}\) NMR spectroscopy, XRD and thermal analysis. They concluded that heating of C-S-H results in increasing polymerization and structural disorder, and decreasing basal-spacing. Thomas and Jennings\textsuperscript{13-15}, from the study of the effect of heat treatment on the pore structure and drying shrinkage of type I Portland cement paste, concluded that heating of cement paste causes a change in the pore-size distribution, with an increase in capillary porosity and a decrease in mesoporosity due to a densification of the C-S-H gel phase associated with increased polymerization of the silicates and the release of liquid water.
For everything above mentioned, it is possible to deduce that there is enough information on the influence of the temperature on the microstructure and in particular on the SA, porosity and pore-size distribution of the Portland-based materials. But there is not information about the changes induced by the temperature on the hydration of belite cement and in particular the fly ash belite cements (FABC).

So, the main aim of the present paper is to study the changes, caused by heating at 40ºC for 180 days under saturated water vapor atmosphere, of two types of fly ash belite cements, called FABC-2-N (in which, a previous alkaline hydrothermal treatment of the fly ash was carried out) and FABC-2-W (in which, a previous hydrothermal treatment in demineralised water of the fly ash was carried out). The changes caused on the C-S-H were investigated at a nanoscale (1-100 nm) by measuring the pore-size distribution and specific surface area by means of the sorption isotherms of nitrogen gas and the BET method. At a microscale the porosity and pore-size distribution was measured by mercury intrusion porosimetry. The influence of the results on those corresponding to the mechanical compressive strength was also studied. The results were compared with those obtained at 20ºC in equivalent fly ash belite cements\textsuperscript{16, 17}.  

II. Experimental Procedure
Spanish coal fly ash of high Ca content (ASTM Class C) called FA-2, was used as a raw material. The chemical composition of the starting fly ash and cements (Table I) was determined according to the Spanish standard UNE-EN 196-2.

The fabrication process of the fly ash belite cement, called FABC-2, has two steps. A mixture of FA-2 and commercial CaO at a Ca/Si molar ratio of 2 was firstly hydrothermally treated in 1M NaOH solution (or demineralised water) at a solution-to-solid ratio of 3:1, for 4 h at the temperature of 200°C with continuous stirring and 1.24 MPa pressure. The solid obtained after filtration was 3 times washed with demineralised water to eliminate the excess of NaOH. In a further step, the dried solid (80°C over night) was heated at a rate of 10°C/min up to 600°C and at 5°C/min from 600°C to 800°C. The chemical compositions of the two cements, called FABC-2-N and FABC-2-W for NaOH 1M solution and demineralised water, respectively, are given in Table 1. More characterization details can be found in reference 9.

Pastes were prepared at a demineralised water-to-cement ratio of 0.82 and 0.68 for FABC-2-N and FABC-2-W, respectively, with a commercial water reducer additive (Rheobuild-1000) in a proportion of 2% (by weight of cement). After mixing, series of 6 prisms were molded into 1x1x6 cm specimens and compacted by vibration. The samples were demolded after 1 day at > 95% rh and cured at 40°C under > 95% rh in sealed containers for a period ranging from 1 to 180 days from mixing.
The compressive mechanical strength was measured in every series of 6 samples. Then, a part of samples were cut in monolithic pieces of about 7 mm. The gel characterization at a nanoscale (1-100nm) was evaluated from the BET surface area and pore-size distribution analysis. The monolithic pieces of about 7 mm were previously dried at room temperature in desiccators with silica gel, up to a constant weight, to eliminate free water (evaporable water) and then about 0.5 g of sample was degasified at 50ºC (to prevent decomposition of C-S-H gel) under vacuum up to reach 5 μm Hg pressure.

The hydrothermal treatment was carried out with a Parr model 4522 (1000 mL pump with split-ring closure and a PID model 4842 temperature controller). XRD patterns were recorded on a Philips PW 1730 diffractometer with Cu Kα1 radiation. Surface-area measurements were made by the BET multipoint method (Model ASAP 2010, Micromeritics Instrument Corp., Norcross, GA), using N2-77 K gas. The surface areas were calculated from the sorption isotherm data, using the BET method18, in the relative pressure range of 0.003-0.3. Pore volume and pore-size distributions were calculated according to the Barret-Joyner-Halenda (BJH) method19, using data from the adsorption isotherm branch. The porosity and pore-size distribution were investigated by mercury intrusion porosimetry carried out with a Micromeritics Pore Sizer IV 9600 V1.05, in the pressure range of 0.5-33000 psia. SEM analysis was performed with a Jeol 5400 instrument equipped with an energy dispersive X-ray spectroscopy module (EDS) Oxford ISIS model. The samples were covered with carbon by sputtering. SEM/EDX semiquantitative analyses were made with an accelerating
voltage of 20 KV and a reference current of 300 $\mu$A on powder samples for determining the alkaline, alkaline-earth: iron oxides, alumina, silica and sulphur content. The EDX microanalysis has been carried out in spot mode over each different crystalline phase, being the limit detection of 0.2%.

### III. Results

**1) Surface area and mechanical strength**

For normal curing, the evolution with time of compressive strength and surface area are similar and adjusted to a direct logarithmic function for the two FABC-2-W and FABC-2-N cements (Fig. 1). The temperature of 40ºC increased, at early ages of hydration, the gain rate of both the compressive mechanical strength and surface area, which were markedly higher than those obtained at normal curing. Nevertheless, the temperature of 40ºC caused a decrease of both the compressive mechanical strength and surface area after 28 days of hydration.

The main difference between the two belite cements was the hydration rate, which was faster at early ages, in the case of FABC-2-N in comparison with that of FABC-2-W. This deduction was made from the higher values of the two parameters measured.

Given that the major contribution to the surface area is due to the C-S-H gel and that it is the responsible of the mechanical properties, quantitative correlations are expected to be found among them, as can be seen in Fig. 2,
where a direct linear regression is obtained for normal curing. The slope is markedly higher in the case of FABC-2-N. When the curing was carried out at 40ºC, the points are located, in general, to the right of the line, indicating higher surface area values for a given compressive strength, or lower compressive strength for a given surface area value.

These quantitative correlations are very useful tools for the prediction of the mechanical behaviour of new materials such as the fly ash belite cement here studied, and validate the nanostructural data obtained from adsorption isotherms of N₂-77, which are directly related to C-S-H gel development.

(2) Pore-size distribution from sorption isotherms

To explain and understand the changes induced by the temperature on the C-S-H gel, its pore-size distribution was measured at a nanoscale (1 to 100 nm) from the adsorption of N₂ gas, after 180 days of hydration. In general, two ranges of pore sizes are well defined by the peaks centred at about 3nm and 12 nm of diameters (Fig. 3). As can be seen, the temperature influences the C-S-H pore-size distribution; At 40ºC, the intensity of the peak centred at 12 nm decreased as that of the peak centred at 3 nm increased. This behavior indicated a refinement of the C-S-H gel pores.

IV. Discussion

The decrease of the mechanical compressive strength in both belite cements (FABC-2-W and FABC-2-N) caused by the temperature of 40ºC is in apparent
contradiction with the refinement of the C-S-H gel pore structure showed in Fig. 3.

This behaviour is also supported by the results of Jennings et al.\textsuperscript{13} on hydrated type I Portland cement cured at 60\(^\circ\)C. The authors, on the basis of a previous work\textsuperscript{12}, explained that the temperature caused an increase of the degree of polymerization in the C-S-H gel according to oxolation reactions and liberation of one water molecule:

\[
-Si-OH + HO-Si- \rightarrow -Si-O-Si- + H_2O
\]

The loss of water increased the C-S-H density being also responsible of the increase of larger capillary pores. If that is true, in our case, the increase of larger capillary pores could justify the loss of compressive strength of Fig. 1.

As Paul and Glasser stated\textsuperscript{11}, another effect caused by the temperature, which could increase the amount of larger capillary pores, is the conversion of low density paste constituents to higher-density katoite \((\text{Ca}_3\text{Al,Fe})_2\left(\text{SiO}_4\right)_{3-x}(\text{OH})_{4x}\), which is not normally developed at 25\(^\circ\)C. This is also produced in the case of FABC, as can be seen in Fig. 4, where cubic katoite \((\text{Ca}_3\text{Al}_2\text{Si}_4\text{O}_{10})(\text{OH})_8\) is formed in both pastes but with higher intensity in the case of the FABC-2-N.

Between 10 and 12 of the 2\(\theta\) angular zone, two reflections appeared which correspond the first to the basal space of hydrated calcium-monosulpho-aluminate \(\left[\text{Ca}_2\text{Al(OH)}_6\text{H}_2\text{O}\right]_2\text{SO}_4\cdot8\text{H}_2\text{O}\), which shifted to higher values perhaps
due to carbonation and formation of the hydrated calcium-monocarbo-aluminate ([Ca$_2$Al(OH)$_6$H$_2$O]$_2$CO$_3$·9H$_2$O), both of the hexagonal lamellar AFm structural family$^{20}$.

Besides, Paul and Glasser$^{11}$ observed that the composition of the C-S-H gel changed with the temperature: The Si/Ca molar ratio increased from 0.58 at 25$^\circ$C to 0.66 at 85$^\circ$C (if only Ca and Si are reckoned). This decreasing ratio effectively liberates calcium which is incorporated in other phases, mainly katoite. In our case, very similar Si/Ca atom ratio is obtained for the C-S-H gel of FABC-2-W (0.57 at 20$^\circ$C and 0.69 at 40$^\circ$C), and, therefore, one can expect that the liberated Ca is incorporated in the katoite.

The aspect of dense katoite zones, hexagonal plates together with C-S-H and microcraks formed in the dried paste, which could increase the larger capillary pores, can be seen in Fig. 5. The microcracks could be formed by the shrinkage due to the exhaustive drying of samples during its preparation for examination in the microscope and for obtaining the gas adsorption-desorption isotherms.

Given that both mechanisms, the formation of katoite and polymerization of C-S-H gel as well as the cracks converge in the formation of larger capillary pores, we decide to measure that type of pores from mercury intrusion porosimetry.
As can be seen in Fig. 6, in the case of FABC-2-W paste, the total porosity decreased with hydration time from 46% after 7 days to 34% (by weight) after 180 days; more relevant changes were produced in the pore-size distribution, where the amount of pores of diameter $>0.05\ \mu m$ strongly decreased over hydration time (from 30.3% to 2.8% after 7 and 90 days, respectively), whereas the amount of pores of diameter $<0.05\ \mu m$ strongly increased (from 15.2% to 32.5% after 7 and 90 days, respectively). From 90 days to 180 days, the behaviour is opposite: an increase of larger pores is produced (from 2.8% to 9.6%), whereas the amount of pores of diameter $<0.05\ \mu m$ decreased (from 32.5% to 24.2%).

The porosity of FABC-2-N pastes is markedly lower at early ages, compared with that of FABC-2-W (30% vs 46% after 7 days), but from 28 days of hydration, the amount of bigger pores ($>0.05\ \mu m$) is considerably higher. The percentage of these pores increased over time from 8.2% to 19.6% as those corresponding to diameter lower than 0.05 $\mu m$ decreased from 23.3% to 16.9%, justifying the loss of mechanical strength.

V. Conclusions

- Parallel evolution of compressive strength and surface area with hydration time is produced at early ages of hydration for the two FABC-2-W and FABC-2-N belite cements.
• The temperature of 40°C caused, at early ages, compressive mechanical strength and surface area values markedly higher than those obtained at 20°C, nevertheless, at later age of hydration the temperature caused a decrease of the compressive mechanical strength, but no for the surface area.

• In the case of FABC-2-W, a densification of the C-S-H gel was produced at the temperature of 40°C, which favored the formation of pores of \( \sim 3 \text{ nm} \) of diameter leading to higher surface area values, compared with the C-S-H gel formed at 20°C. In the case of FABC-2-N, the densification of the gel was less evident. Nevertheless, the temperature of 40°C caused an increase of capillary porosity (>0.05 \( \mu \text{m} \)) at later age of hydration and, consequently, a decrease of compressive mechanical strength.

• The temperature of 40°C favoured the formation of more dense cubic katoite \((\text{Ca}_3\text{Al}_2(\text{SiO}_4)(\text{OH})_6)\) at later ages of hydration, which is more evident for the FABC-2-N.

• Significant direct linear quantitative correlations were found among the nanostructure characteristics of the C–S–H gel and macro structural engineering property such as the compressive mechanical strength for the two FABC-2-W and FABC-2-N cements under normal conditions. At 40°C, the correlations were not so clear probably due to another microstructural factor such as the increase of larger capillary porosity (>0.05 \( \mu \text{m} \)) and formation of cracks.
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| Table I. Chemical Composition of the Starting Fly Ash (FA-2) and anhydrous FABC-2-W and FABC-2-N cements (% by weight). |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                                | LOI’             | CaO             | SiO₂             | Fe₂O₃ (total)   | Al₂O₃           | MgO             | SO₃             | Na₂O            | K₂O             | SiO₂* (reactive) | BET (m²/gr)     |
| 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            |

*LOI = loss on ignition; *Silica reactive according to Spanish standard UNE-80-224
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