

Effect of curing temperature in the hydration of a belite cement with high level of fly ash

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ABSTRACT

This study aimed to determine the physical, mechanical, mineral and microstructural properties of a industrially manufactured hybrid cement (HYP), consisting 47,5 % Belite clinker + 47,5 % FA + 5 % solid alkaline activator. The effect of the curing temperature (25°C, or 85 °C) on hydration kinetics and on compressive strength development (in paste prisms and mortar prisms) was determined. Isothermal conduction calorimetry shows that curing at 85°C, accelerates relevantly the hydration process. The 3 days compressive strength achieved by curing at 25oC was 9 MPa, but 30 MPa was the mechanical strength after 3 days if mortars were cured at 85°C. After 28 days, the compressive strength of the specimen cured at 25oC was 33 MPa, and 43 MPa after 90 days. The specimens cured at 85oC exhibited a slightly better compressive strength. The hydration products formed were characterized using XRD, SEM/EDX and 27Al and 29Si MAS-NMR. The main reaction product formed was found to be a mixture of cementitious gels: C-(A)-S-H /C-A-S-H/(N,C)-A-S-H. The initial curing at 85°C for 20 h inhibited the formation of ettringite (or favored its rapid decomposition), at least during the first 90 days (maximum age of the materials analyzed in this work). On the contrary, curing at 85°C favors the precipitation of the sulphates in the form of Phase U

1. INTRODUCTION

OPC concrete is the most used material, after water, by humans. Its widespread use is essentially due to the availability, in a large part of the planet, of the raw materials necessary for its manufacture; also to the good “quality/price” ratio, and naturally to its good technological properties (Biernacki, *et al* 2017). However, due to the high level of OPC consumption worldwide, the Portland cement manufacturing process entails a serious environmental problem related to the high emissions of greenhouse gases into the atmosphere; also with the high consumption of fossil fuels and finally with the large consumption of mineral resources (Scrivener *et al* 2018). Therefore, cement manufacturers and the scientific community have been working for years on the development of low energy Clinkers (Belitic Clinker, for example) and/or on the development of cements with a low Clinker factor (pozzolanic cements, hybrid alkaline cements, etc.) (Chatterjee, *et al* 1996; Malhotra and Mehta, 1996; García-Lodeiro *et al.* 2013a,2013b, Alahrache, *et al.* 2016). In fact the interest in the belitic cements goes back to the beginning of 1970. Common Portland clinker is usually produced having more than 60% of Alite and about 15%-20% of Belite. In order to reduce the consumption of energy and the CO₂ emissions during the fabrication of Clinker we can try to increase the Belite content and simultaneously to reduce the Alite fraction (Martín-Sedeño, *et al* 2010). However, the Belite cement has a serious drawback: The velocity of hydration of C₂S is too slow, which makes the initial development of mechanical resistance to be poor.

On the other hand, alkaline cements (also called geopolymers) are characterized by not including Clinker in its composition (Palomo *et al.* 2014; Luukkonen *et al.* 2018). Alkaline cements, in fact, are obtained by the chemical reaction between silicoaluminous materials (having amorphous or vitreous nature) and some alkaline product. The main reaction product is a gel type N-A-S-H (Fernández-Jiménez and Palomo, 2005); and the type of secondary products that can be identified in alkaline cements varies depending on the chemical composition of the precursor, the alkaline activator (nature and concentration) and the curing conditions (Duxson, *et al.* 2005; Hajimohammadi, *et al.* 2010 and 2011; Fernández-Jiménez, *et al* 2005, 2006 and 2017).

In this work, the mixture of both types of cement is proposed: A Belite Cement and an Alkaline Cement, in order to give birth to a Hybrid Alkali Cement. Specifically, a dosage is proposed: 47.5% of Belite Clinker + 47.5% of fly ash (FA) + 5% of an alkaline activator in solid state. This cement after hydration with water sets and hardens. The ultimate goal of the research was to determine the effect of the curing temperature (25°C or 85°C) on the hydration kinetics of said Hybrid Cement as well as on the development of mechanical strength and on the nature of the hydration products.

2. EXPERIMENTAL

2.1 Material

The Belite cement used to make the "alkaline-belitic" hybrid cement was manufactured in a regular Portland cement plant (with exclusive research purposes). The programmed composition of the hybrid alkaline cement was 47.5% of Belite clinker + 47.5% of flying ash + 5% of solid activator. This cement has been called HYP. The 5% solid activator consisted of a cocktail of alkaline salts with a predominance of Na₂SO₄. The cement was made in a ball mill. Some thousand tons were prepared. The chemical composition and the mineralogy composition of the cement are presented in Table 1.

Table 1. Chemical composition (wt %) and cement mineralogy of HYP

Chemical composition	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	SO ₃	Na ₂ O	K ₂ O	TiO ₂	MnO/Mn ₂ O ₃	Other ^a	LoI
%	29.1	38.5	14.9	4.93	2.18	3.26	1.61	1.61	0.86	0.04	0.27	2.82
Mineralogy	C ₃ S	C ₂ S	C ₃ A	C ₃ AF	C ₁₂ A ₇	Gypsum	Activator	Quartz	Mullite	Amorphous		
%	8.10	24.0	1.30	3.00	1.10	1.20	1.60	4.00	3.80	52.0		

^aLol, Losson Ignition (1000 °C)

The chemical composition of HYP was determined by X-ray fluorescence (Bruker S8 TIGER) and the quantitative mineral composition was determined by DRX (BRUKER AXS D8 ADVANCE), applying the Rietveld method. The mineral analysis showed a Clinker and Activator content somewhat lower than the programmed one and a higher content of fly ash. These variations were associated with a low crystallinity of some clinker phase (*Sánchez-Herrero et al 2019*) and also with small errors in the dosing process. The particle size distribution of HYP was determined by laser granulometry (SYMPATEC diffractometer with a measuring range of 0.90-175 microns). 96.5% of the particles were found to be smaller than 45 µm and more than 40% smaller than 10 µm, (see Figure 1).

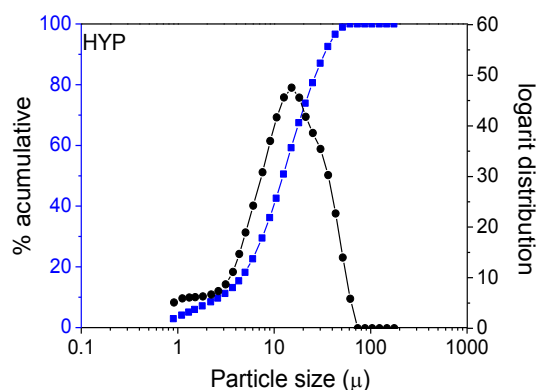


Figure 1. Particle size distribution of HYP

2.2 Method

HYP cement was used to prepare prismatic mortar specimens according to EN 196-1 (4 × 4 × 16 cm), with a "water/cement" ratio = 0.5 and "sand/cement" ratio = 3. In order to determine the effect of the curing temperature on the hydration of HYP, two curing temperatures were applied to the hybrid cement paste: a) Ambient temperature: 25°C and 99% RH for 20 h; b) 85°C and 99% RH for 20 h. (*Palomo et al. 2014; Qu, et al 2016*). After this initial curing period, the specimens (all of them) were extracted from the molds and stored in a curing chamber (25°C ± 1°C and 99% RH) till the testing age (3, 28 or 90 days). For the materials characterization paste samples with a "water/cement" ratio = 0.3 were prepared. At the testing age the hydration was stopped by freezing the material with acetone/ethanol. The mineral and microstructural characterization was carried out with different instrumental techniques: X-ray diffraction (XRD) using a Philips diffractometer, CuKα 1.2 radiation with a step time of 0.5 s; Electron microscopy (SEM/EDX) using a JEOL JSM scanning electron microscope equipped with a solid state BSE detector and an energy dispersion X-ray analyzer LINK-ISIS (EDX); Nuclear magnetic resonance in solids (NMR MAS) using a Bruker Avance-400 spectrometer (²⁷Al: 104.3 MHz, rotation speed, 10 kHz, 200 acquisitions, reference, [Al(H₂O)₆]³⁺, ²⁹Si: 79.5 MHz, rotation speed, 10 kHz, 1,000 acquisitions, reference TMS). The rate of heat of hydration of the cured cements at the two tested temperatures was determined by isothermal conduction calorimetry (THERMOMETRIC TAM).

3. RESULTS AND DISCUSSION

3.1 Reaction kinetics

The hydration rate and the total heat released by the two hybrid cements (respectively cured at 25°C and 85°C) were determined by isothermal conduction calorimetry (see Fig. 2). In both curves of Fig. 2 an initial pre-induction peak has been detected, but the signal occurs so quickly that the measurement cannot be done accurately. After a very short induction period, the presence of a double peak is observed both in the material cured at 25°C and in the one cured at 85°C. At 25°C, an intense peak is observed at the age of 4.9 h. and a second small one at 8.9h. According to the bibliography (*Shi, and Day, 1995; Escalante-Garcia and Sharp, 2000 and 2001;*

(Garcia-Lodeiro, et al 2013a; Donatello, et al. 2014) the first peak is normally related to the precipitation of the main reaction products and the second peak might be related to the formation of ettringite. The fact that HYP contains only 8.1% of C_3S , 24% of C_2S and a high content of fly ash makes the total heat released by this cement to be relatively low (130 J/h). When the cement is hydrated at 85°C, again two peaks are observed: one little signal at 3.5 h. and a second intense one at 4.6 h. The total heat released in this case is 380 J/h which is associated with a high level of reactivity (clinker phases react and fly ash reacts from the very beginning of the hydration).

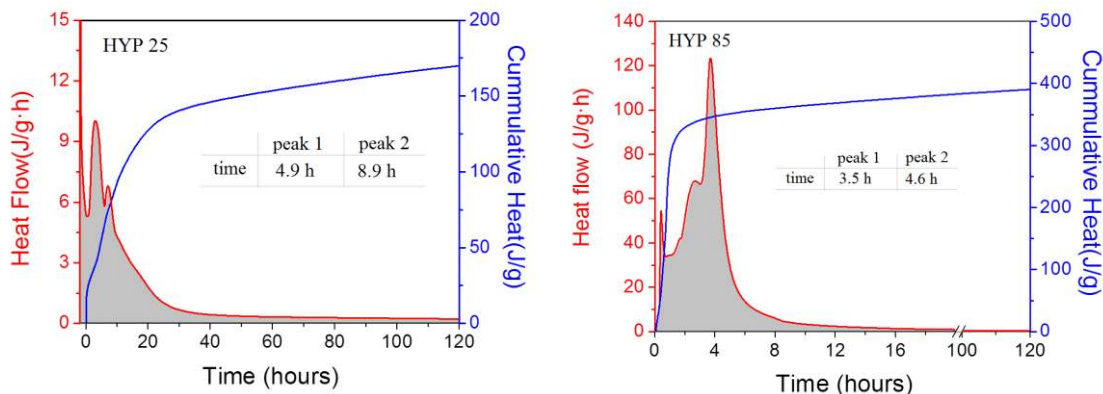


Figure 2. Heat flow and total heat released by HYP pre-cured at 25 or 85 °C

3.2 Mechanical strength

Fig. 3 describes the development of compressive strength in HYP mortars and pastes (two curing temperatures and all the tested ages). Mortars and pastes cured at 25°C have relatively low compressive strengths at 3 days (9 MPa and 20 MPa respectively). However, these values progress over time: the mortars reach 33MPa after 28 days, and 43 MPa after 90 days. A similar behavior is observed in the pastes (see Fig. 3 (b)), where 60MPa are reached after 90 days. According to European Standards, HYP could be classified as Type 32.5N cement. The initial curing temperature (25°C or 85°C) significantly affects the initial compressive strength: 30 MPa at 3 days in mortars and 45 MPa in pastes. In contrast, the development of mechanical strength at longer time (28 and 90 days) was very slow in materials cured at 85°C; much slower than mortars and pastes cured at room temperature. These results indicate that the curing temperature has an effect in the hydration of HYP cement similar to that observed in the hydration of OPC under similar thermal conditions (Escalante-García, and Sharp, 2000 and 2001).

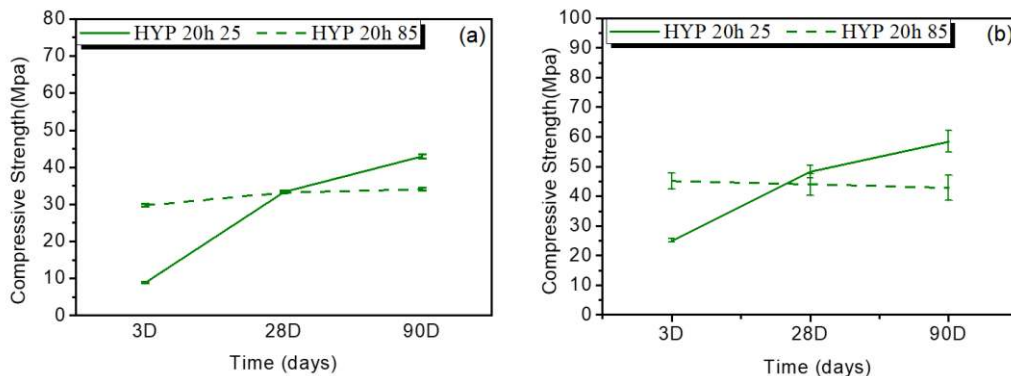


Figure 3. Compressive strength of HYP corresponding to: (a) mortar and (b) paste. Tests

were run at two curing temperatures and 3 ages (3, 28 and 90 days).

3.3 Mineral and microstructural characterization

Figure 4 shows the XRD patterns of the anhydrous HYP and the hydrated pastes at 3, 28 and 90 days (both, HYP cured at 25°C and also at 85°C). The starting HYP shows several signals associated with the presence of alite, belite, tricalcium aluminate and ferritic phase (clinker phases). The intensity of these peaks decreases as a function of the hydration time. The diffractogram pattern of the anhydrous HYP also presents peaks associated with mullite and quartz-like phases associated with fly ash included in HYP. These signals do not vary in intensity neither by the time of hydration nor by the curing temperature. It is important to note that in the hydrated cement pastes no portlandite is detected; however, the presence of calcite and some carboaluminates is observed. The amount of calcite formed in the pastes at 25°C is greater than in pastes cured at 85°C. Comparing the diffractogram patterns of pastes cured at 25°C and 85°C, a very interesting difference has been observed: at 25°C the ettringite signal is detected, while at 85°C the sulphates precipitate in the form of phase U. Phase U is a calcium sulfoaluminate containing a certain amount of sodium in the microstructure. Its morphology is very similar to the one of calcium monosulphoaluminate (Dosch, and Strassen, 1967; Li, et al. 1996).

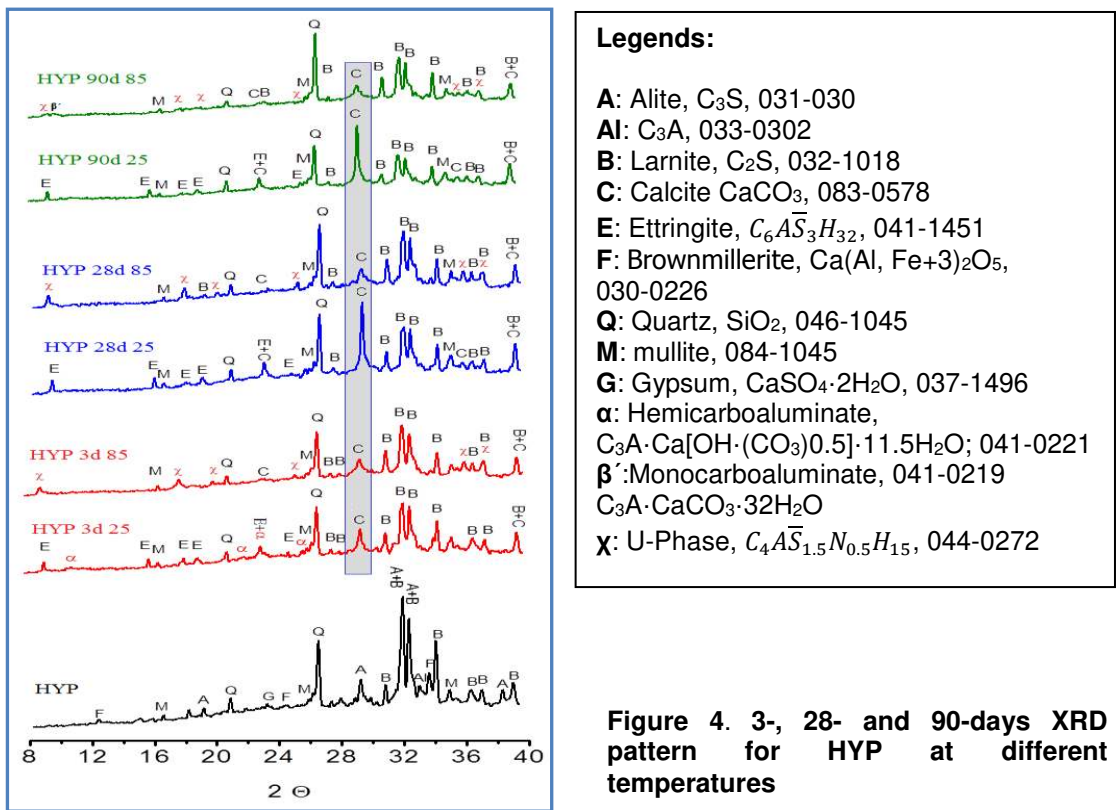


Figure 4. 3-, 28- and 90-days XRD pattern for HYP at different temperatures

The anhydrous HYP and the hydrated pastes after 28 days were selected for analysis through MAS-NMR. In Fig. 5, all selected HYP spectra (^{27}Al and ^{29}Si MAS-NMR) are shown. The ^{27}Al spectrum of anhydrous HYP presents a wide and asymmetric signal centered at +54 ppm together with a shoulder at +80 ppm, both associated with Al(IV). The deconvolution of this signal shows that it is formed by the sum of three components: + 62 ppm and + 47 ppm, both related to the content of tetrahedral aluminum in fly ash (Fernández-Jiménez, et al 2006), and the + 80 ppm signal associated with Al τ in the Clinker phases (Colombet, and Grimmer, 1994). Additionally, a very low intensity signal centered around + 2 ppm is observed in the spectrum. It is mainly associated with the presence of Al(VI) in the mullite of the fly ash (Fernández-Jiménez, et al 2006). When HYP is hydrated, the spectrum of ^{27}Al is remarkably modified. As far

as the Al(IV) signal is concerned, the +80 ppm shoulder disappears completely while the wide signal centered at +54 ppm shifts to + 58 ppm. On the other hand, there appears some very sharp and intense signals between +15 and 0 ppm associated with the formation of phases having Al(VI). The changes observed in the area of Al(IV) are associated both with the reaction of the clinker phases and with the reaction of the fly ash. The A_T present in the Clinker phases is transformed in A_O after clinker hydration; but the Al of the ash is considered will be a part of the cementing gels (it means no changes in the coordination of the Al). By deconvolution of the spectra, the wide signal centered at +58 ppm is broken down into three signals that appear around +68 +59 and + 47 ppm. The first is associated with the presence of A_T in type C-(A)-S-H or C-A-S-H gels (Andersen, et al 2003; Richardson, 2014). The signal of +59 ppm is interpreted as due to the presence of A_T in type gels (C, N)-A-S-H or N-A-S-H (although the contribution of A_T present in the ash can not be excluded even without reacting); and with respect to the signal of +47 ppm this can be associated with the aluminum present in the ash, even without reacting (Garcia-Lodeiro et al 2010a and 2010b).

As far as the Al(VI) signal is concerned, the deconvolution shows that said signal is also formed by the sum of several signals. In the case of the paste cured at 25°C, the overlapping of three signals respectively centered on +13.21, +9.05 and +6.09 ppm is detected. The first two signals, of great intensity, are respectively associated with the presence of A_O in ettringite and AFm phases. The signal of low intensity centered at +6.09 ppm is associated with the remains of A_O present in mullite together with the possible formation of a non-crystalline Aluminum Hydroxide (not detected by XRD) similar to Gibbsite [this phase is commonly referred to in the bibliography as the third aluminate hydrate (TAH)] (Andersen, et al 2006). When the curing temperature was 85°C, the deconvolution of the wide signal centered at + 9.4 ppm indicates the overlapping of two signals: one centered at +10.2 ppm and the other one at +2.5 ppm. The first could be related to the presence of phase U and/or AFm phases (detected by XRD). The signal of low intensity centered at +2.5 ppm again is associated with the presence of A_O either of mullite or in TAH. These results confirm those observed by XRD: Curing temperature seems to decisively influence the type of calcium sulfoaluminate formed in these cements.

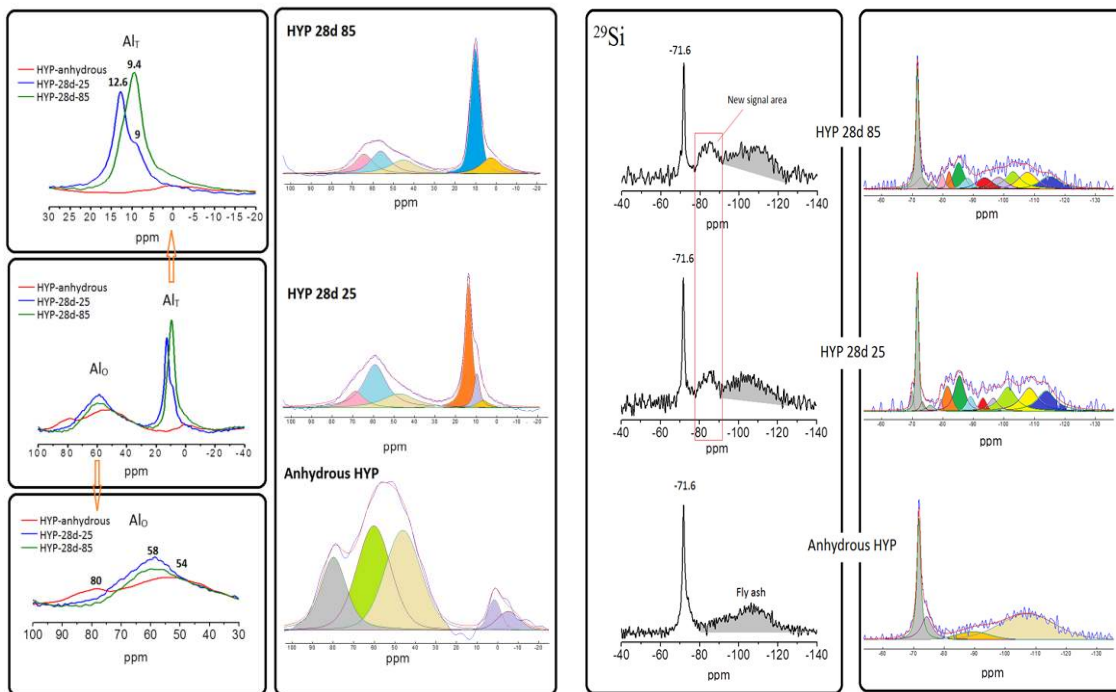


Figure 5. ²⁷Al and ²⁹Si MAS-NMR spectra for the anhydrous HYP and its 28-day pastes pre-cured at 25 °C and 85 °C

The ^{29}Si MAS-NMR spectrum of anhydrous HYP shows a narrow and symmetric signal centered at -71.6 ppm, which is related to the belite content in the clinker and which is almost overlapped with a wide signal at -74 ppm, associated with the presence of C_3S (see Figure 5). One more signal of low intensity is also observed between -80 ppm and -120 ppm; it is associated with the presence of silicon in the fly ash (Fernández-Jiménez *et al.* 2006). When the cement is hydrated, it is observed that the intensity of the signals associated with the anhydrous phases (Clinker and ash) decrease and new signals appear; especially in the area between -80 and -90 ppm. These new signals are associated with the formation of the hydration products. The deconvolution of these spectra again shows the overlapping of different signals. In the 25°C paste spectrum, the presence of several signals centered at -79 ppm, -82 ppm and -85 ppm can be observed. They can be respectively associated with the presence of Q^1 , Q^2 (1Al) and Q^2 (0Al) units (Andersen, *et al.* 2003; Richardson, 2014), which are normally identified in gel C-(A)-S-H. However, other signals appear at more negative shifting: -89 , -93 , -95 and -101 ppm; these signals can be associated with both, the presence of units Q^3 (mAl) and Q^4 (mAl). The authors of this work consider that this group of signals can be associated with the possible formation of a mixture of gels C-A-S-H and/or (N,C)-A-S-H (gels with more polymerized structures than the CSH gel formed in a paste normal OPC) (García-Lodeiro *et al.* 2010a and 2010b, Myers *et al.* 2013, 2015). The signals appearing at more negative values (-108 ppm) are related with different crystalline forms of SiO_2 in the ash (i.e. quartz (Fernández-Jiménez *et al.* 2006).

When HYP pastes were cured at 85°C for 20 h., the spectrum of ^{29}Si (hydration age =28 days) is relatively similar to that of 25°C . New signals appear again centered at -79 ppm -82 and -85 ppm indicating the formation of gels C-(A)-S-H or C-A-S-H. At more negative ppm we observe the appearing of signals at -88 , -93 , -98 and -103 ppm. They are associated with Q^3 (mAl) as Q^4 (mAl) units in gels C-A-S-H and/or (N, C)-A-S-H. Although the ^{27}Al spectra showed clear differences in the type of curing (25°C or 85°C), the poor resolution obtained in the spectra of ^{29}Si makes it difficult to draw conclusions, except that in both pastes it seems very probable the formation of a mixture of gels.

3.4 SEM - EDX study

The SEM/EDX analysis on the 28-day pastes (cured at 25°C and 85°C) is described in Figure 6. In both cases a fairly compact matrix is observed associated to the formation of a mixture of cementing gels coexisting with unreacted ash particles. The EDX analysis of the matrix shows that it is mainly composed of calcium and silicon together with some aluminum and some sodium (see points 1, 2, 3, 4). The percentage of these elements varies locally: near the ash particles the composition of the gel is rich in Si and Al and poor in Ca, but close to the OPC particles (still unreacted particles) or in zones where an OPC particle was reacting, the gel is rich in Ca and poor in Al. These results confirm that a mixture of gels [C-(A)-S-H/C-A-S-H/(NC)-A-S-H] is being formed as it has been explained for some other hybrid cements (García-Lodeiro, *et al.* 2016, Alahrache, *et al.* 2016). The small sodium content in the gel is coming from the solid alkaline activator added to the HYP. This element becomes a part to the structure of the gel in order to balancing the charge deficit that occurs when Al in the gel is replacing Si. The EDX results also show the presence of a small amount of sulphates likely adsorbed on the surface of the gel. Scientific literature about the up-taking of sulfate ions on the C-S-H surface reports that this adsorption is favored by the presence of alkalis and high curing temperatures (Fu, *et al.* 1994; Thomas, *et al.* 2003). Nonetheless, the impact of the sulfate ions absorbed into the gel structure has yet to be determined. In contrast, the risk posed by the release of sulfate at mature cement ages is better understood.

In summary, the results described in this work show that it is possible to produce belitic cements with high contents of fly ash (and using an alkaline activator) within a real and viable technological context. The results obtained by calorimetry and XRD show that increasing the initial curing temperature (25°C or 85°C in the first 20 hours) involves some acceleration in the early hydration of HYP. This likely explains the good mechanical strength development after 3 days (≈ 30 MPa in mortars and 45 MPa in pastes). However, at longer reaction times, the beneficial effect of a high curing temperature is (85°C) is considerably attenuated. This may be due to the fact that reaction products, that formed rapidly at 85°C , will rise a compact barrier around the unreacted particles, which hydration will be delayed (Escalante-García, and Sharp,

2000 and 2001). The NMR and EDX results are clearly indicating that a mixture of C-(A)-S-H/C-A-S-H/(N,C)-A-S-H gels is being formed at 28 days. The differences due to the curing temperature are observed in the formation of some secondary reaction products. Curing at 25 °C involves the precipitation of sulfates (in the form of Aft), while at 85 °C the formation of U phase was observed. This can be due to two causes: i) on one hand the curing temperature destabilizes the formation of ettringite; ii) the curing temperature increases the solubility of sodium sulphate used as activator, increasing more rapidly the Na content (and pH) in the medium, which favors the stabilization of the U phase instead of ettringite.

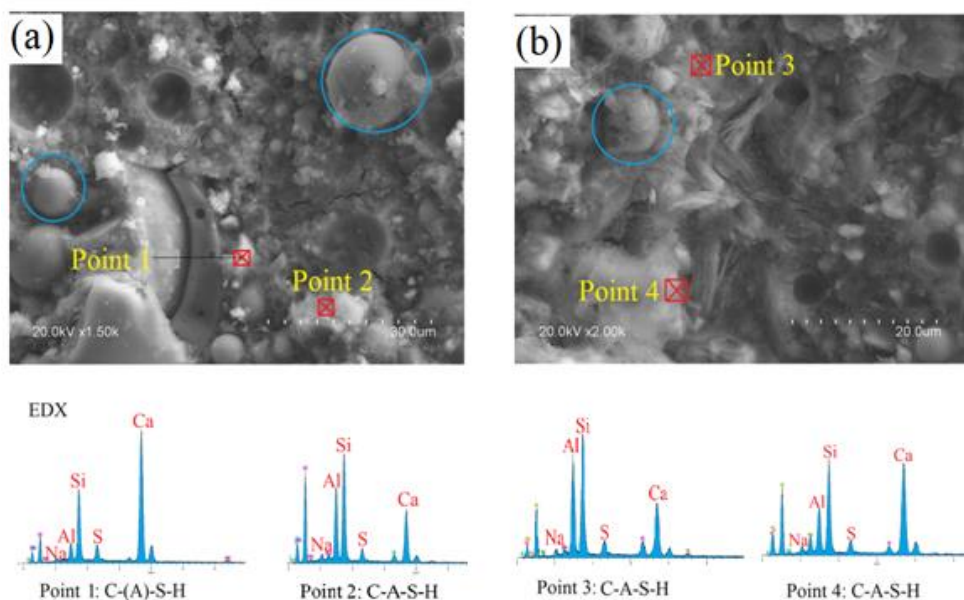


Figure 6. SEM micrographs and EDX analysis of 28-day HYP pre-cured at: (a) 25 °C; (b) 85 °C

4. CONCLUSIONS

This work shows that it is possible to make a cement from a Belite Clinker and a high content of fly ash and a solid activator in low concentrations (<5%). This cement is able to set and harden giving rise to a material with good mechanical performance. The mechanical strength development is due to the formation and precipitation (as the main reaction product) of a mixture of cementitious gels C-(A)-S-H /C-A-S-H/(N,C)-A-S-H. These gels contain a higher percentage of aluminum and are more polymerized than the traditional C-S-H gel. In hybrid cement, a high curing temperature accelerates hydration reactions in the same way as in OPCs and also like in alkaline cements developing quick mechanical strength. However, the subsequent development of the mechanical strength is slower than when the cement is cured at room temperature. The initial curing at 85°C for 20 h inhibited the formation of ettringite (or favored its rapid decomposition), at least during the first 90 days (maximum age of the materials analyzed in this work). On the contrary, curing at 85°C favors the precipitation of the sulphates in the form of Phase U.

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