

# Materials and Structures

## Influence of Fly Ash blending on hydration and physical behavior of Belite-Alite-Ye'elimate cements --Manuscript Draft--

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	Ministerio de Economía, Industria y Competitividad, Gobierno de España (IEDI-2016-0079)	Dr. Isabel Santacruz
<b>Abstract:</b>	<p>A cement powder, composed of belite, alite and ye'elimate, was blended with 0, 15 and 30 wt% of fly ash and the resulting blended cements were further characterized. During hydration, the presence of fly ash caused the partial inhibition of both AFt degradation and belite reactivity, even after 180 days. The compressive strength of the corresponding mortars increased by increasing the fly ash content (68, 73 and 82 MPa for mortars with 0, 15 and 30 wt% of fly ash, respectively, at 180 curing days), mainly due to the diminishing porosity and pore size values. Although pozzolanic reaction has not been directly proved there are indirect evidences.</p>	
<b>Response to Reviewers:</b>	<p>Comments from the editors and reviewers:</p> <p>Editor in Chief summary: this is a valid article that needs minor revisions to be published. Please provide a point-by-point reply to the reviewer and a revised manuscript in which all modifications are clearly marked. In addition, please improve the language.</p> <p>Associate Editor: I am happy to request minor revisions on the basis of the detailed</p>	

review comments received. However, it is important that the authors seek language assistance from either a professional editing service or a native English-speaking colleague, to fully revise the grammar and language usage throughout the manuscript.

Reviewer #1: Thank you for submitting an interesting and well-researched article that furthers the understanding of the interactions of fly ash in BAY cements. The following are comments to help you improve the paper.

1. The grammar of the manuscript needs to be edited, as there are numerous grammatical mistakes throughout the manuscript, but particularly in the introduction. Some of the initial mistakes include:

Abstract: Cement should be cements; three is plural.

Answer: The sentence has been modified.

“A cement powder, composed of belite, alite and ye’elimate, was blended with 0, 15 and 30 wt% of fly ash and the resulting cements were further characterized.”.

Moreover, the full abstract has been revised and slightly modified.

Introduction first page:

Line 37: Change coal-firing to coal-fired; Change from power station perspective to From the power station's perspective.

Answer: Corrected.

Line 42: Change building industry perspective to building industry's perspective.

Answer: Corrected.

Line 52: Change ultimate strength increase to increased ultimate strength.

Answer: Corrected.

Your defined acronym is PC not OPC.

Answer: Corrected.

Line 54: Add a in front of high amount

Answer: This sentence has been modified.

“[...] and the maximum amount of FA that can be added.”

Line 60: Change emission to emissions, and change on to of.

Answer: Done

Introduction second page:

Line 7: Cements is plural, use have, not has.

Answer: The abstract has been modified.

Line 24: Add comma after, C4A3\$.

Answer: Done

Line 37: PC not OPC, add a in front of pozzolanic and filler

Answer: Done

Line 39: Change to focused on the effects of FA on....

Answer: Done

Line 52: Add "the" in front of phase.

Answer: Done

Please carefully read the manuscript and correct the grammar errors throughout.

Answer: The manuscript has been checked carefully and grammar errors have been modified.

2. The clinker mineralogy is key to this study since it determines what hydration products are capable of forming. I would move it out of the supplementary section.

Answer: Done. We agree with the reviewer that the initial mineralogy of the cement and the FA is key to understand their hydration. We have moved Table S1 to Table 1.

Consequently, to fulfill the limited number of figures and tables in the manuscript, we

have moved old table 2 to supplementary section, now Table S1. "The heat released during the hydration of all samples, prepared without and with SP, was also measured. The results taken at 5 and 24 hours are given in Table S1, deposited as electronic supplementary material. It is clear that the addition of 0.5 wt% of SP (referred to the solid content) provokes a delay in the hydration and consequently less heat is released in all the systems at any time."

3. Does w/c & w/s include correction for moisture in the superplasticizer?

Answer: Yes, the moisture of the superplasticizer was taken into consideration to prepare pastes and mortars at the desired w/c and w/s ratios. Now in the manuscript, we have included a new sentence to clarify this. "The moisture of the superplasticizer was considered for the preparation of cement pastes and mortars."

4. Section 3.3, you get around to discussing the Ca toward the end of this section and how excess CH should not be stable with AH3 and should promote AFm at the expense of AFt; however when I first read through this section I kept thinking that you were highlighting the wrong points and only got around to the real issues which is BAY cements are more calcium rich and will promote more AFm phase formation and less AH3 and AFt due to mass balance/thermodynamic stability. You might consider rearranging this section a bit, but strictly speaking it is ok.

Answer: We have highlighted the reaction of ye'elimite in the presence of portlandite and reorganized the full paragraph. Now in the manuscript: "On the one hand, ye'elimite reacts with anhydrite and water to form ettringite and amorphous aluminum hydroxide [54]; however, in the presence of portlandite, ye'elimite will react to give only ettringite [53]. This portlandite comes from the early hydration of C3S that will also yield C-S-H gel. Consequently, crystalline aluminum hydroxide (called gibbsite) or crystalline portlandite were not detected by LXRPD, see inset in Figure 4. Furthermore, crystalline portlandite was only found in FA0BAY, by TGA-DTG, after 28 hydration days, where a small peak was detected at 450°C, Figures 3 and S3 (the latter deposited as supplementary electronic material). These results are in agreement with Winnefeld & Lothenbach [55] where portlandite was not detected in related systems. Portlandite, in these types of pastes, seems to initially favor the formation of ettringite [53]. Later, in the absence of calcium sulfate and ye'elimite (after 24 h), portlandite reacts with AH3 and ettringite to produce AFm-type phases [52, 56]. This will justify the reduction of the AFt amount and the increase of AFm-type phase contents, from 28 to 180 days of hydration in FA0BAY, Table 2. Moreover, the hydration of C3S and  $\beta$ -C2S have yielded a silicate-rich hydration environment in which AFt is unstable [24, 49] and stratlingite and katoite are formed [46, 57]. Consequently, the presence of stratlingite in FA0BAY paste at 1 day, and in FA15BAY and FA30BAY pastes at 7 days, is noticeable. This is in agreement with the thermal analysis of FA#BAY (w/c=0.40). In all cases, two typical decomposition events were found: i) the first one, at ~110 °C, corresponds to the dehydration of C-S-H and AFt [53, 58, 59]; these two processes are strongly overlapped and consequently, these results cannot be directly compared to those obtained by LXRPD. ii) The second group of signals corresponds to the dehydration of AFm-types phases: between 120 and 180 °C, which is associated with the dehydration of monosulfoaluminate [50, 59], and between 180 and 220°C is associated with the dehydration of stratlingite [16, 32, 60]. As mentioned before, the hydration of alite yields portlandite and favors the formation of AFt during the first hydration hours [53, 59, 61], so CH was not detected by TGA, as expected, in agreement with Winnefeld & Barlag [59], Trauchessec et al. [52] and Hargis et al. [56]."

5. Section 3.3, You have a higher degree of hydration of belite at lower w/c?

Answer: The referee is right we have obtained a slightly higher degree of reaction of belite in the sample with lower w/c in the cement without FA. However, the value obtained after 28 days are low, and the one after 90 days is very similar, and between the error of this calculation. Consequently, and in order to highlight that the important result here is that the low degree of reaction is not a consequence of a lacking of water, we have rewritten this paragraph, now in the manuscript; "The main result obtained by this test is that the degree of reaction of belite in FA0BAY is almost the same, in spite of the w/c, and reached ~45% at 90 days."

6. Section 3.3, you found that stratlingite formed preferentially at a higher w/c ratio, this is in agreement with the recently published paper, "The effect of water and gypsum

	<p>content on strätlingite formation in calcium sulfoaluminate-belite cement pastes" You should cite it, since both yours and their findings are fairly new on this detail of CSA cement hydration.</p> <p>Answer: Done. This has been included in the text. "This is in agreement with Jeong et al. [62], who found that stratlingite content increased in CSA cements by increasing the w/c ratio.</p> <p>As the referee suggested, a new reference has been included as [62]. Remaining references have been renumbered.</p> <p>62. Jeong Y, Hargis CW, Chun SC, Moon J (2018) The effect of water and gypsum content on strätlingite formation in calcium sulfoaluminate-belite cement pastes. <i>Constr Build Mater</i> 166:712–722 . doi: 10.1016/j.conbuildmat.2018.01.153</p> <p>7.The figures that I received were pixelated, so please just check them on your final submission.</p> <p>Answer: All the figures have been deposited as high resolution Tiff files. They could be downloaded from the link of the top-right corner of the pdf file.</p> <p>8. I cannot recall definitive proof of CSH in a BAY cement previously. You may want to check the literature again and emphasize this point a bit more if you guys are indeed the first to show it.</p> <p>Answer: We can state that C-S-H gel is formed by NMR and DTG results. However, we are not the first ones showing it. We have cited two articles where the authors proved the formation of C-S-H gel in similar systems. Now in the manuscript "The formation of C-S-H gel in similar systems has also been reported by Shoude et al. [69] and Xin et al. [70]." The two new references are:</p> <p>69. Shoude W, Cheng C, Lingchao L, Xin C (2012) Effects of slag and limestone powder on the hydration and hardening process of alite-barium calcium sulphoaluminate cement. <i>Constr Build Mater</i> 35:227–231 . doi: 10.1016/j.conbuildmat.2012.03.004.</p> <p>70. Xin C, Jun C, Lingchao L, et al (2004) Study on the hydration of Ba-bearing calcium sulphoaluminate in the presence of gypsum. <i>Cem Concr Res</i> 34:2009–2013 . doi: 10.1016/j.cemconres.2004.02.021</p> <p>9. The FA in CSA cement study by Ioannou et al. had 2 papers, please cite both. Thank you for the 67 references that you do include, it does reflect well on your manuscript and shows the activity in this field.</p> <p>Answer: Done. As the referee suggested, an Ioannou et al. work in FA + CSA has been included as [36]. Remaining references have been renumbered.</p> <p>36. Ioannou S, Reig L, Paine K, Quillin K (2014) Properties of a ternary calcium sulfoaluminate-calcium sulfate-fly ash cement. <i>Cem Concr Res</i> 56:75–83 . doi: 10.1016/j.cemconres.2013.09.015</p> <p>Authors comments: We have noticed that old references #49 and #59 were the same. This error was corrected.</p>
<b>Additional Information:</b>	
<b>Question</b>	<b>Response</b>
Provide the total number of words in the manuscript (excluding figure caption and table caption)?	6605
Provide total number of FIGURES?	The total number of figures is 6. However, figure 2 is a multi pack figure (two figures) and Figure 5 is a multi pack figure (three figures). Consequently, 9 figures should be considered.
Provide total number of TABLES?	4

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# **Influence of Fly Ash blending on hydration and physical behavior of Belite-Alite-Ye'elimite cements**

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Cement nomenclature: C=CaO, S=SiO<sub>2</sub>, A=Al<sub>2</sub>O<sub>3</sub>, F=Fe<sub>2</sub>O<sub>3</sub>,  $\bar{S}$ =SO<sub>3</sub> and H=H<sub>2</sub>O

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2  
3 **Abstract**  
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6 A cement powder, composed of belite, alite and ye'elinite, was blended with 0, 15 and 30 wt% of fly ash  
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8 and the resulting blended cements were further characterized. During hydration, the presence of fly ash  
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10 caused the partial inhibition of both AFt degradation and belite reactivity, even after 180 days. The  
11  
12 compressive strength of the corresponding mortars increased by increasing the fly ash content (68, 73 and  
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14 82 MPa for mortars with 0, 15 and 30 wt% of fly ash, respectively, at 180 curing days), mainly due to the  
15  
16 diminishing porosity and pore size values. Although pozzolanic reaction has not been directly proved there  
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18 are indirect evidences.  
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23 **Keywords**— Belite-alite-ye'elinite cement; Fly ash; Hydration; Rietveld method; Phase evolution; NMR;  
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25 Compressive strength.  
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32 **1. Introduction**  
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35 An environmental strategy to reduce the negative effect of the CO<sub>2</sub> footprint of the Portland Cement (PC)  
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37 industry consists on its partial substitution by reactive industrial by-products, such as fly ash [1, 2]. Fly ash  
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39 (FA) is the major solid waste generated from coal-fired power stations. From the power station's  
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41 perspective, there are methods to exploit fly ash disposal in an economically advantageous way. From the  
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43 building industry's perspective, FA is looked upon as a supplementary cementitious material (SCM) which  
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45 is used in mass as a cement replacement material [3]. Furthermore, the addition of FA to cement can  
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47 modify its properties, such as reduced hydration heat and thermal cracking in concrete at early ages,  
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49 durability, enhanced ultimate strength, and improved workability of fresh mortar/concrete when cement is  
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51 replaced by FA [3, 4]. Despite the benefits offered by PC cement/concrete blended with FA, there are  
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53 some limitations related to the variability of the mineralogy and chemical composition of the FA [5], and  
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55 the maximum amount of FA that can be added.  
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3 Another alternative to reduce CO<sub>2</sub> emissions consists of the development of eco-cements composed by less  
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5 calcite demanding phases, such as belite and ye'elimite. That is the case of calcium sulfoaluminate (CSA)  
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7 clinkers that, in general, contain 50 to 70 wt% of ye'elimite (C<sub>4</sub>A<sub>3</sub>S̄)<sup>1</sup>, and other phases such as belite and  
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9 calcium aluminates [6–10]. Their main hydration products are ettringite, monosulphoaluminate and  
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11 aluminum hydroxide [11–16]. Nowadays, belite-ye'elimite-ferrite (BYF) cements have been studied as  
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13 potential substitutes of PC [15, 17–22]. The mineralogical composition of BYF clinkers/cements includes  
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15 belite and ye'elimite as main and secondary phases, respectively. Since the reactivity of β-C<sub>2</sub>S is slow,  
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17 these materials may develop low mechanical strengths at early ages. A possible solution to this problem  
18  
19 goes through the production of cements composed by belite jointly with alite and ye'elimite, known as  
20  
21 belite-alite-ye'elimite (BAY) cements [23–29]. In these types of systems, the main hydration products are  
22  
23 ettringite, monosulphoaluminate, C–S–H gel, C<sub>3</sub>ASH<sub>4</sub> (silicon hydrogarnet or katoite) and C<sub>2</sub>ASH<sub>8</sub>  
24  
25 (stratlingite). CH and/or AH<sub>3</sub> can also be formed, depending on the C<sub>3</sub>S and C<sub>4</sub>A<sub>3</sub>S̄ ratio [23–25].  
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27 According to the hydration products, the reaction of alite and ye'elimite with water yield to the  
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29 development of high mechanical strengths at early ages, while belite contributes to later values [23, 25].  
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31 The inclusion of FA in BAY cements reduces the environmental impact and improves the performance of  
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33 fresh and hardened states, but this has not been studied yet. From previous studies, it is known that the  
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35 addition of fly ash to PC plays an important role as a pozzolanic addition and as a filler [1–3, 5, 30, 31].  
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37 Recent studies, focused on the effects of FA on CSA cements [32–36], have demonstrated that FA works as  
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39 both a filler and a dilutor.

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42 The aim of this work is to study the hydration and mechanical properties of a blended BAY cement with 0,  
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44 15 and 30 wt% of FA. The present study helps to understand the effect of FA on the mechanisms of BAY  
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46 hydration and its impact on the mechanical strengths. The characterization of these cement pastes has been  
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58 <sup>1</sup> Cement nomenclature will be used in the whole manuscript: C=CaO, S=SiO<sub>2</sub>, A=Al<sub>2</sub>O<sub>3</sub>, F=Fe<sub>2</sub>O<sub>3</sub>, S̄=SO<sub>3</sub>, M=MgO and  
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60 H=H<sub>2</sub>O.  
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2 performed by Rietveld quantitative phase analysis (RQPA) to determine the phase assemblage during  
3 hydration, rheological measurements, isothermal calorimetry, thermogravimetric analysis and magic-angle-  
4 spinning nuclear-magnetic resonance spectroscopy. Finally, the mechanical properties of the corresponding  
5 BAY blended mortars were measured.  
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## 12 2. Experimental

### 13 2.1. Materials

#### 14 2.1.1. Blended BAY cements with Fly Ash.

15 BAY cement was produced as published elsewhere [23]. Blended cements were produced by mixing the  
16 BAY cement for 60 minutes in a micro-Deval machine at 100 rpm, without balls, with 15 and 30 wt% of  
17 Class F fly ash. FA was supplied by the power station of Lada (Spain) [35]. Blended cements will be  
18 henceforth labeled as FA0BAY (without any addition), FA15BAY and FA30BAY (with 15 and 30 wt% FA,  
19 respectively), and their general name will be FA#BAY. Table 1 shows the mineralogical composition  
20 (including amorphous and non-quantified crystalline phases, ACn) of BAY cement and FA powders,  
21 determined through RQPA combined with the internal standard methodology, as detailed below. The three  
22 studied cements showed similar Blaine values,  $\sim 5250 (\pm 100) \text{ cm}^2/\text{g}$ , where the differences are within the  
23 measurement error. The particle size distribution of the three cements and fly ash was measured by laser  
24 diffraction (Mastersizer S, Malvern, UK) and is shown in Figure S1, deposited as electronic supplementary  
25 material. The three cements show a trimodal behavior, where the median particle size by volume ( $D_{v50}$ )  
26 slightly increase with the presence of fly ash, as expected, being  $\sim 4$ ,  $\sim 5$  and  $\sim 6 \mu\text{m}$  for FA0BAY, FA15BAY  
27 and FA30BAY, respectively.  
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#### 52 2.1.2. Cement Paste Preparation

53 Cement pastes were prepared with deionized water using a water-to-cement (w/c) mass ratio of 0.40,  
54 following UNE-EN 196-3 standard. Thus, FA0BAY, FA15BAY and FA30BAY pastes show water/solid  
55 (w/s) of 0.40, 0.34 and 0.28, respectively. To improve the workability, a polycarboxylate-based  
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2 superplasticizer (SP) (Floadis 1623, Adex Polymer S.L., Madrid, Spain), with 25 wt% of active matter, was  
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4 added to the pastes (from 0.2-0.6 wt% of active matter referred to the solid content). The moisture of the  
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6 superplasticizer was considered for the preparation of cement pastes and mortars. Moreover, FA0BAY and  
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8 FA30BAY cements were selected to be hydrated at a w/c ratio of 0.57, with the aim of understanding the  
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10 w/c effect (the latter has a w/s of 0.40). All pastes were cast into hermetically closed cylinders of  
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12 polytetrafluoroethylene (PTFE), volume of 2.8 cm<sup>3</sup>, and rotated during the first 24 h, at 16 rpm, at 20 ± 1°C  
13  
14 [37]. Afterward, all samples were removed and kept within water at 20 ± 1°C. The hydration of cement  
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16 pastes at a w/c of 0.40 was arrested as detailed in [35] at 1, 7, 28, 90 and 180 days of curing ages, and the  
17  
18 hydration of pastes at a w/c of 0.57 was arrested at 28 and 90 curing days.

### 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65

#### 1.1.3. Cement Mortar Preparation

All cement mortars were prepared according to UNE-EN196-1 at cement/sand and w/c of 1/3 and 0.40,  
respectively, with the optimum amount of superplasticizer. CEN EN196-1 standard sand was used. Cubes  
(3 × 3 × 3 cm<sup>3</sup>) were cast and cured at 20 ± 1 °C and 99% relative humidity (RH) for 24 h; then the cubes  
were demolded and cured in a water bath at 20 ± 1 °C until testing (compressive strength) at the same  
curing ages than pastes were characterized (1, 7, 28, 90 and 180 days).

## 2.2. Characterization

### 2.2.1. Rheological behavior

Pastes for rheological characterization were prepared by mechanical stirring with helices according to  
EN196-3:2005 standard procedure. The rheological behavior of the pastes was studied using a viscometer  
(VT550 Model, Thermo Haake, Karlsruhe, Germany) with a serrated coaxial cylinder sensor, SV2P,  
provided with a cap to reduce evaporation. Flow curves were obtained under controlled rate (CR)  
measurements. Firstly, the shear rate was increased from 0 to 100 s<sup>-1</sup> with ramp times of 6 s, for a total of

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2 11 ramps. Secondly, the shear rate was decreased from 100 to 0 s<sup>-1</sup> following the same ramp times. Before  
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4 starting the rheological measurement, the pastes were pre-sheared for 30 s at 100 s<sup>-1</sup>.  
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### 7 2.2.2. Isothermal Calorimetric study

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10 An eight channel TAM Air Isothermal Calorimeter (TA Instruments, USA) was used to measure the heat  
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12 flow at 25°C during 72 h. An automatic admix device was used to mix the powder samples with water  
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14 inside the calorimeter for 2 minutes in order to avoid any data loss at the beginning of the reaction. To  
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16 understand the superplasticizer effect on the early hydration and heat flow, the anhydrous powder cement  
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18 (2 g) was hydrated at a w/c of 0.40 with and without SP. The heat flow of three separate runs for each  
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20 cement was recorded during 72 h according to ASTM C1679 – 13. No significant differences were  
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22 observed between the three runs, so the arithmetic average was used.  
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### 27 2.2.3. Laboratory X-ray powder diffraction (LXRPD) data collection and analysis

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29 Powder patterns for the anhydrous cements and stopped pastes were recorded on a D8 ADVANCE (Bruker  
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31 AXS, Germany) diffractometer (BRUKER), located in SCAI at University of Malaga (Spain), using  
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33 monochromatic MoK $\alpha_1$  radiation ( $\lambda = 0.7093 \text{ \AA}$ ) [Ge (111) primary monochromator] with LYNXEYE XE  
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35 500  $\mu\text{m}$  linear dispersive energy detector, optimized for high-energy radiation, with the maximum opening  
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37 angle. This diffractometer works on transmission geometry and samples are placed between kapton foils  
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39 and are rotated at 10 rpm during data collection. Data were collected from 3° to 35° (2 $\theta$ ). To determine the  
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41 amorphous and crystalline non-quantified (ACn) content, an internal standard approach was employed [38,  
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43 39]. As internal standard, Quartz (99.56%, ABCR GmbH & Co. KG), was added to the samples to a total  
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45 content of ~20 wt%. The mixtures (sample-standard) were homogenized for 15 min in an agate mortar. In  
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47 addition, an in-situ LXRPD study of FA0BAY with and without superplasticizer was performed to  
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49 understand its effect on early hydration. To do so, LXRPD were collected on the same D8 ADVANCE  
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51 diffractometer by using an Anton Paar MHC-trans chamber. Data were collected at 25°C and relative  
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53 humidity (RH) value of 95%. These X-ray diffraction patterns were collected every 15 min. All patterns  
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2 were measured between 2° and 27° (2 $\theta$ ) with a step size of 0.017° and counting time of 0.5 s per step (total  
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4 time per pattern 8 minutes).

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7 All the patterns were analyzed by the Rietveld method using GSAS software package [40] by using a  
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9 pseudo-Voigt peak shape function [41] with the asymmetry correction included [42] to obtain RQPA. The  
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11 refined overall parameters were: phase scale factors, background coefficients, unit cell parameters, zero-  
12  
13 shift error, peak shape parameters and preferred orientation coefficient, if needed (March–Dollase  
14  
15 ellipsoidal preferred orientation correction algorithm [43]). The crystal structure descriptions used for all  
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17 phases were given in references [44] and [45], and updated crystallographic descriptions were used for  
18  
19 stratlingite [46], orthorhombic [47] and pseudo-cubic [48] ye'elimite.

#### 20 21 22 23 24 25 2.2.4. *Thermal analysis*

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28 Thermogravimetric (TGA) and differential thermogravimetric (DTG) analyses were performed in a SDT-  
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30 Q600 analyzer (TA instrument, New Castle, DE) for a ground fraction (~30 mg) of every paste after the  
31  
32 hydration was arrested. The samples were heated up to 1000°C at a heating rate of 10 °C/min.  
33  
34 Measurements were carried out in an open platinum crucible under air flow (100 mL/min). The weight loss  
35  
36 from RT to 600°C was computed to be chemically bounded water (used to calculate the free water (FW)  
37  
38 content of the pastes), and that from 600 to 1000°C was considered as CO<sub>2</sub>.

#### 39 40 41 42 43 2.2.5. *Mercury intrusion porosimetry (MIP) analysis*

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46 MIP has been employed to characterize the pore structure (open porosity and pore size distribution) of  
47  
48 FA#BAY cement pastes at 180 curing days, for the sake of comparison. The cylindrical specimens (15 mm  
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50 length and 10 mm diameter) were first immersed in isopropanol for 72 h, and then dried at 40°C until the  
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52 weight loss of the samples was stable. The surface of this cylinder was removed prior to the analysis. A  
53  
54 Micromeritics Autopore IV 9500 instrument (Micromeritics Instrument Corporation, Norcross- GA, US)  
55  
56 was used, and the pressure applied by the intrusion porosimetry ranged from 0 to 300 MPa. A constant  
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58 contact angle  $\theta$  of 130° was assumed for data evaluation.  
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## 2.2.6. Solid state Magic Angle Spinning Nuclear Magnetic Resonance (MAS-NMR)

Solid state  $^{27}\text{Al}$  and  $^{29}\text{Si}$  MAS-NMR spectra were recorded on a Bruker AVIII HD 600 NMR spectrometer, located at SCAI at University of Malaga (Spain), (field strength of 14.1 T) at 156.4 MHz with a 2.5 mm triple-resonance DVT probe using zirconia rotors at 20 and 15 kHz spinning rates (respectively for  $^{27}\text{Al}$  and  $^{29}\text{Si}$ ).  $^{27}\text{Al}$  experiment was performed with (Hpedec) and without (One pulse)  $^1\text{H}$  decoupling by applying a single pulse ( $\pi/12$ ), an excitation pulse of 1  $\mu\text{s}$ , 5.0 s relaxation delay and 200 scans. The chemical shift was referenced to an external solutions of 1 M of  $\text{Al}(\text{NO}_3)_3$ .  $^{29}\text{Si}$  MAS-NMR experiments were performed with  $^1\text{H}$  decoupling (cw sequence) by applying a single pulse ( $\pi/2$ ), an excitation pulse of 5  $\mu\text{s}$ , 30 s relaxation delay and 10800 scans. The chemical shift was referenced to an external solution of tetramethylsilane (TMS).

## 2.2.7. Compressive strengths

The compressive strength of cubic mortars ( $3 \times 3 \times 3 \text{ cm}^3$ ) was measured in a Model Autotest 200/10 W (Ibertest, Spain) press. Three cubic mortars were tested, at every studied hydration age, to obtain the standard deviation values according to UNE-EN196-1. A corrector factor was applied to the obtained values to be compared with standard prisms ( $4 \times 4 \times 16 \text{ cm}^3$ ).

# 3. Results and discussion

## 3.1. Rheological study

A good dispersion of fresh cement pastes and mortars is **necessary** to prepare homogeneous specimens. To achieve that, the preparation of pastes/mortars with the right amount of SP is essential, mainly when low water contents are used. Here, the addition of SP was optimized through the rheological behavior of the cement pastes. Figure S2, deposited as electronic supplementary material, shows the flow curves of the cement pastes prepared with 0, 15 and 30 wt% of fly ash, respectively ( $w/c=0.40$ ) with different SP contents. Pastes without SP could not be measured due to their high viscosity values. In general, by adding SP, the viscosity of all pastes decreased to a minimum value, which corresponds to the optimum amount.

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2 From there, the viscosity of all pastes was kept constant or even slightly increased. This can be seen on  
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4 detail in Figure 1, where the deflocculation curves of all pastes, taken from the up-curves at the shear rate  
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6 of  $100 \text{ s}^{-1}$ , are shown. In the case of the FA0BAY family, pastes with 0.5 and 0.6 wt% SP show the lowest  
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8 viscosity values and show similar rheological behaviors (Figures 1 and S2), where the paste with 0.5 wt%  
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10 viscosity values and show similar rheological behaviors (Figures 1 and S2), where the paste with 0.5 wt%  
11  
12 SP shows the smallest thixotropic cycle (58 and 157 Pa/s for pastes with 0.5 and 0.6 wt%, respectively). In  
13  
14 the case of the FA15BAY family, pastes with 0.5 and 0.6 wt% SP also show the lowest viscosity values, and  
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16 identical rheological behaviors (similar thixotropic cycle), Figure S2. Finally, in the FA30BAY family, the  
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18 paste with 0.5 wt% SP shows the lowest viscosity value (Figures 1 and S2) and, when the SP content was  
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20 increased up to 0.6 wt%, the viscosity slightly increased. Thus, in all cases, 0.5 wt% of SP was selected as  
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22 the optimum SP content for further studies. In addition, the viscosity of the pastes increased by increasing  
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24 the FA content, Figure 1, due to the higher solid content (same w/c, but different w/s ratios) as described in  
25  
26 the Experimental section.

### 27 28 29 30 31 32 *3.2. Effect of the superplasticizer on FA0BAY early-age hydration*

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34 In-situ LXRPD of the FA0BAY paste was performed to determine the phase assemblage within the first  
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36 hours of hydration; the obtained results were correlated with the heat flow. Figure 2 shows the in-situ  
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38 RQPA results and heat release measured by isothermal calorimetric for FA0BAY prepared without SP  
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40 (Figure 2a) and with 0.5 wt% SP (Figure 2b). The heat released during the initial period, 0-0.2 h, is mainly  
41  
42 assigned to the partial dissolution of anhydrite, mayenite, alite and ye'elimite, and the initial precipitation  
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44 of AFt [13, 49, 50]. The difference in the intensity of the heat flow between both pastes at the initial period  
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46 is likely due to the effect of superplasticizer on the rate of both phase dissolution and formation of hydrates;  
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48 it is known that polycarboxylates have a retarder effect on the hydration of cement pastes [51]. After 5  
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50 minutes of hydration, the sample without SP reaches a maximum heat flow of  $0.052 \pm 0.008 \text{ W/g}$ , while the  
51  
52 sample with SP reaches about half of it ( $\sim 0.024 \pm 0.001 \text{ W/g}$ ). Once the initial period is finished, the rate  
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54 of the heat evolution and phase dissolution can be described by a pronounced exothermic peak in Figure 2a  
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56 and a shoulder in Figure 2b centered at 8 hours of hydration in both figures. In both cases, alite dissolves at  
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2 a slower rate than ye'elimite, as expected [23, 49, 52, 53]. The most interesting result of this study is that  
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4 the addition of SP has mainly retarded the dissolution of anhydrite and, to a lower extent, of C<sub>12</sub>A<sub>7</sub>,  
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6 meanwhile ye'elimite dissolves at the same rate in both pastes.  
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10 The heat released during the hydration of all samples, prepared without and with SP, was also measured.  
11  
12 The results taken at 5 and 24 hours are given in Table S1, deposited as electronic supplementary material. It  
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14 is clear that the addition of 0.5 wt% of SP (referred to the solid content) provokes a delay in the hydration  
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16 and consequently less heat is released in all the systems at any time.  
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### 20 3.3. Hydration study of FA#BAY cements.

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23 The hydration behavior of all cement pastes, after arresting hydration, was also studied at different curing  
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25 ages. Table 2 gives the RQPA results of pastes hydrated at 1, 3, 7, 28, 90 and 180 days, including ACn and  
26  
27 free water (FW) contents. Figures 3 and 3S (the latter deposited as electronic supplementary material) show  
28  
29 the TGA-DTG plots for FA0BAY, FA15BAY and FA30BAY cement pastes at all curing ages. All pastes  
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31 were prepared with 0.5 wt% SP, as optimized before. Figure 4 shows Rietveld plots of FA15BAY at 180  
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33 days (w/c=0.40), with peaks labeled, as a representative example. From Table 2, it can be observed that  
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35 C<sub>4</sub>A<sub>3</sub> $\bar{5}$  and C<sub>3</sub>S phases have been totally dissolved after 1 and 7 days of hydration, respectively, in all  
36  
37 cements. On the one hand, ye'elimite reacts with anhydrite and water to form ettringite and amorphous  
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39 aluminum hydroxide [54]; however, in the presence of portlandite, ye'elimite will react to give only  
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41 ettringite [53]. This portlandite comes from the early hydration of C<sub>3</sub>S that will also yield C-S-H gel.  
42  
43 Consequently, crystalline aluminum hydroxide (called gibbsite) or crystalline portlandite were not detected  
44  
45 by LXRPD, see inset in Figure 4. Furthermore, crystalline portlandite was only found in FA0BAY, by  
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47 TGA-DTG, after 28 hydration days, where a small peak was detected at 450°C, Figures 3 and S3 (the latter  
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49 deposited as supplementary electronic material). These results are in agreement with Winnefeld &  
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51 Lothenbach [55] where portlandite was not detected in related systems. Portlandite, in these types of pastes,  
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53 seems to initially favor the formation of ettringite [53]. Later, in the absence of calcium sulfate and  
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3 ye'elite (after 24 h), portlandite reacts with  $\text{AH}_3$  and ettringite to produce AFm-type phases [52, 56]. This  
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5 will justify the reduction of the AFt amount and the increase of AFm-type phase contents, from 28 to 180  
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7 days of hydration in FA0BAY, Table 2. Moreover, the hydration of  $\text{C}_3\text{S}$  and  $\beta\text{-C}_2\text{S}$  have yielded a silicate-  
8  
9 rich hydration environment in which AFt is unstable [24, 49] and stratlingite and katoite are formed [46,  
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11 57]. Consequently, the presence of stratlingite in FA0BAY paste at 1 day, and in FA15BAY and FA30BAY  
12  
13 pastes at 7 days, is noticeable. This is in agreement with the thermal analysis of FA#BAY ( $w/c=0.40$ ). In all  
14  
15 cases, two typical decomposition events were found: i) the first one, at  $\sim 110^\circ\text{C}$ , corresponds to the  
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17 dehydration of C-S-H and AFt [53, 58, 59]; these two processes are strongly overlapped and consequently,  
18  
19 these results cannot be directly compared to those obtained by LXRPD. ii) The second group of signals  
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21 corresponds to the dehydration of AFm-types phases: between 120 and 180  $^\circ\text{C}$ , which is associated with the  
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23 dehydration of monosulfoaluminate [50, 59], and between 180 and 220 $^\circ\text{C}$  is associated with the  
24  
25 dehydration of stratlingite [16, 32, 60]. As mentioned before, the hydration of alite yields portlandite and  
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27 favors the formation of AFt during the first hydration hours [53, 59, 61], so CH was not detected by TGA,  
28  
29 as expected, in agreement with Winnefeld & Barlag [59], Trauchessec et al. [52] and Hargis et al. [56].  
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34 Belite showed a slow hydration behavior, and only after 28 days, this phase starts its reaction with water in  
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36 FA0BAY, but the reaction of this phase in FA15BAY and FA30BAY is even slower (f.i.  $\beta\text{-C}_2\text{S}$  reacts 41, 25  
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38 and 8% from 28 d to 90 d, for pastes with 0, 15 and 30 wt% FA, respectively). These results might be  
39  
40 justified by the low amount of water used, i.e.  $w/c=0.40$  ( $w/s$  of 0.40, 0.34 and 0.28, for 0, 15 and 30 wt%  
41  
42 of FA, respectively). In order to test this last statement, FA0BAY and FA30BAY pastes were also prepared  
43  
44 at a  $w/c$  of 0.57. Table 3 shows the RQPA results of both pastes at 28 and 90 days. The main result obtained  
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46 by this test is that the degree of reaction of belite in FA0BAY is almost the same, in spite of the  $w/c$ , and  
47  
48 reached  $\sim 45\%$  at 90 days. In addition, the belite hydration has been inhibited in FA30BAY at any  $w/c$ .  
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50  
51 Consequently, the hydration behavior of belite is not influenced by the  $w/c$  under these experimental  
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53 conditions but it seems to be influenced by the addition of FA. Moreover, the  $w/c$  affects the phase  
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55 assemblage, concretely, the katoite/stratlingite. Pastes prepared at  $w/c=0.40$  presented both phases, while  
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2 samples at the w/c of 0.57 only contained stratlingite (see Tables 2 and 3). This is in agreement with Jeong  
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4  
5 *et al.* [62], who found that stratlingite content increased in CSA cements by increasing the w/c.  
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7  
8  $^{27}\text{Al}$  and  $^{29}\text{Si}$  MAS NMR spectra for FA#BAY pastes at 7, 90 and 180 hydration days are shown in Figure  
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10 S4, deposited as electronic supplementary material.  $^{27}\text{Al}$  MAS NMR spectra (Figure S4, left site) shows  
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12  $\text{Al}^{\text{VI}}$  octahedrally-coordinated of ettringite centered at  $\sim 13.5$  ppm [63, 64]. The wide band may be  
13  
14 considered as two resonances, the first one centered at  $\sim 10.5$  ppm assigned to the overlapping AFm-type  
15  
16 phases including stratlingite and monosulfoaluminate [63, 65, 66] and the second one, of less intensity,  
17  
18 centered at  $\sim 9.6$  ppm which is likely due to the aluminium present in the aluminium hydroxide gel. These  
19  
20 signals are common in all pastes at any age [54]. In Figure S4, right site,  $^{29}\text{Si}$  MAS NMR spectra of all  
21  
22 samples showed, at around  $-72$  ppm, a signal corresponding to isolated  $\text{SiO}_4$  tetrahedra ( $\text{Q}^0$  sites) of non-  
23  
24 hydrated belite [64, 67]. In addition, signals located around  $-79$  and  $-84$  ppm, assigned to  $\text{Q}^1$  and  $\text{Q}^2$   
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26 species, are typical of the end and middle chain of  $\text{SiO}_4$  tetrahedra in C-S-H gel, respectively [67, 68]; they  
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28 appear after 90 days in FA0BAY and FA15BAY, although they are very weak in the latter. The presence of  
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30 these signals proves the formation of C-S-H gel from belite reaction in both cements. The formation of C-  
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32 S-H gel in similar systems has also been reported by Shoude *et al.* [69] and Xin *et al.* [70]. However, these  
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34 signals are not present in the FA30BAY spectra, confirming the inhibition of belite reactivity observed by  
35  
36 LXRPD. Moreover, other signals centered at  $-81$  and  $-86$  ppm, asterisk in Figure S4, which correspond to  
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38  $\text{Q}^{2(\text{1Al})}$  and  $\text{Q}^2$  of stratlingite [63, 66], are noticeable at 90 and 180 days in all the cements, although they are  
39  
40 very weak in FA30BAY, corroborating the results obtained by LXRPD given in Table 2. To obtain deeper  
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42 information from these data, the deconvolution of FA#BAY, at 180 hydration days, was carried out (Figure  
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44 5). Here, FA0BAY and FA15BAY at 180 days showed the characteristic  $\text{Q}^1$  and  $\text{Q}^2$  signals of C-S-H,  
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46 although they are slightly weaker in FA15BAY. The hydration of belite and the formation of C-S-H gel at  
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48 later ages has been proven with these results. In addition, these signals were not detected in the FA30BAY  
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50 sample, confirming that the belite hydration was inhibited. In all cements, the characteristic  $\text{Q}^2$  and  $\text{Q}^{2(\text{2Al})}$   
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52 signals of stratlingite were detected, corroborating the results obtained by LXRPD and TGA-DTG.  
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### 3.4. Compressive strength of FA#BAY mortars

Figure 6 represents the compressive strength values of FA#BAY mortars, which increase by increasing both the curing age and the FA content. Table 4 displays the percentages of increase of strength of blended mortars referred to FA0BAY at the same ages. The compressive strength, at 1 day, increased by 15% and 43% for FA15BAY and FA30BAY, respectively, referred to FA0BAY mortar at the same age. This increase in mechanical strengths might have several explanations: i) decrease in porosity; ii) pozzolanic reaction; iii) filler effect. However, the observation of the increase in compressive strengths after 28 days, where there is not a significant belite reaction, could be an indirect evidence of some degree of pozzolanic reaction. Changes in crystalline phase assemblage with time and amount of FA are not high enough to justify this increase in compressive strengths. Consequently, the pore structure of the pastes was studied. The inset of Figure 6 shows the pore size distribution of FA#BAY pastes at 180 hydration days, where the pore size diameter decreases by increasing the FA content. In addition, the open porosity of pastes also decreased by increasing the FA content (16, 13 and 9 vol% for FA0BAY, FA15BAY and FA30BAY, respectively). Thus, the higher compressive strength values can be justified by the lower porosity measured in pastes where higher FA contents are added, mainly due to the filler effect, in agreement with García-Maté et al. [35].

## 4. Conclusions

The addition of a small amount of superplasticizer, 0.5 wt% (of active matter referred to solids), made possible the preparation of homogeneous pastes with low viscosity values (viz. 0.31, 0.42 and 0.71 Pa.s at 100 s<sup>-1</sup> for pastes with 0, 15 and 30 wt% of fly ash). The isothermal calorimetric study reveals that the superplasticizer affects the hydration behavior of calcium aluminate phases in BAY, at early ages, where less heat flow was released. The evolution of all pastes with time was studied through Rietveld quantitative phase analysis, thermal analysis and <sup>27</sup>Al and <sup>29</sup>Si MAS NMR. The presence of fly ash slightly affected the hydration mechanism or kinetics of BAY cement pastes. FA0BAY had slightly different chemical hydration behavior than that of FA15BAY and FA30BAY. In all systems, the main hydration products were AFt,

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2 AFm-phases (monosulfoaluminate and stratlingite), katoite and C-S-H. In silicon and aluminum rich-  
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4 systems, stratlingite and katoite can coexist with C-S-H. In FA0BAY, AFt was unstable from 28 days of  
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6 hydration. Concerning belite hydration, high additions of fly ash inhibited the reactivity of belite. In these  
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8 experimental conditions, we only have found indirect evidence of pozzolanic chemical reaction with FA.  
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10 The increase of water content of these types of systems (w/c from 0.40 to 0.57) affected the  
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12 katoite/stratlingite, i.e. higher w/c yielded to higher contents of stratlingite and lower amounts of katoite.  
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15 Finally, the compressive strengths of these blended mortars increased with the fly ash addition, mainly due  
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17 to the decrease in porosity (and pore size) of the corresponding mortars.  
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33 acknowledged.  
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## 38 Raw data sharing

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40 All powder diffraction raw data files underlying this work can be accessed on Zenodo at  
41  
42 <https://doi.org/10.5281/zenodo.1297485>, and used under the Creative Commons Attribution license.  
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## 47 Compliance with Ethical Standards

48  
49 The authors declare that they have no conflict of interest.  
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3 **Figure Captions**  
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5 Figure 1. Deflocculation curves of FA#BAY pastes at the shear rate of 100 s<sup>-1</sup>.  
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8 Figure 2. Phase evolution during hydration of FA0BAY with w/c=0.40 prepared a) without superplasticizer  
9 and b) with 0.5 wt% of superplasticizer. Isothermal calorimetric Heat Flow curves are shown as black lines.  
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13 Figure 3. Thermogravimetric and differential thermogravimetric analyses (TGA-DTG) of FA0BAY pastes  
14 with w/c = 0.40, prepared with 0.5 wt% of superplasticizer.  
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18 Figure 4. Rietveld plots for FA15BAY with w/c 0.40 at 180 days of hydration using monochromatic  
19 MoK $\alpha_1$ ( $\lambda=0.7093\text{\AA}$ ) radiation. 1 (AFt), 2 ( $\beta$ -C<sub>2</sub>S), 3 (katoite), 4 (stratlingite), 5 (AFm) and 6 (Quartz as  
20 internal standard). The inset shows an enlarged view of a selected-angle region where the absence of  
21 crystalline portlandite or gibbsite diffraction peaks is noticeable.  
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29 Figure 5. Deconvolution of <sup>27</sup>Si MAS-NMR spectra of (a) FA0BAY, (b) FA15BAY and (c) FA30BAY at  
30 180 days. Each spectrum includes experimental (dots) and its deconvoluted spectrum (red line) with  
31 individual contribution of C<sub>2</sub>S (light green line), C-S-H gel (blue and dark green line) and stratlingite (pink  
32 line).  
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39 Figure 6. Compressive strength values of FA#BAY mortars. Inset: Pore size distribution of FA#BAY pastes  
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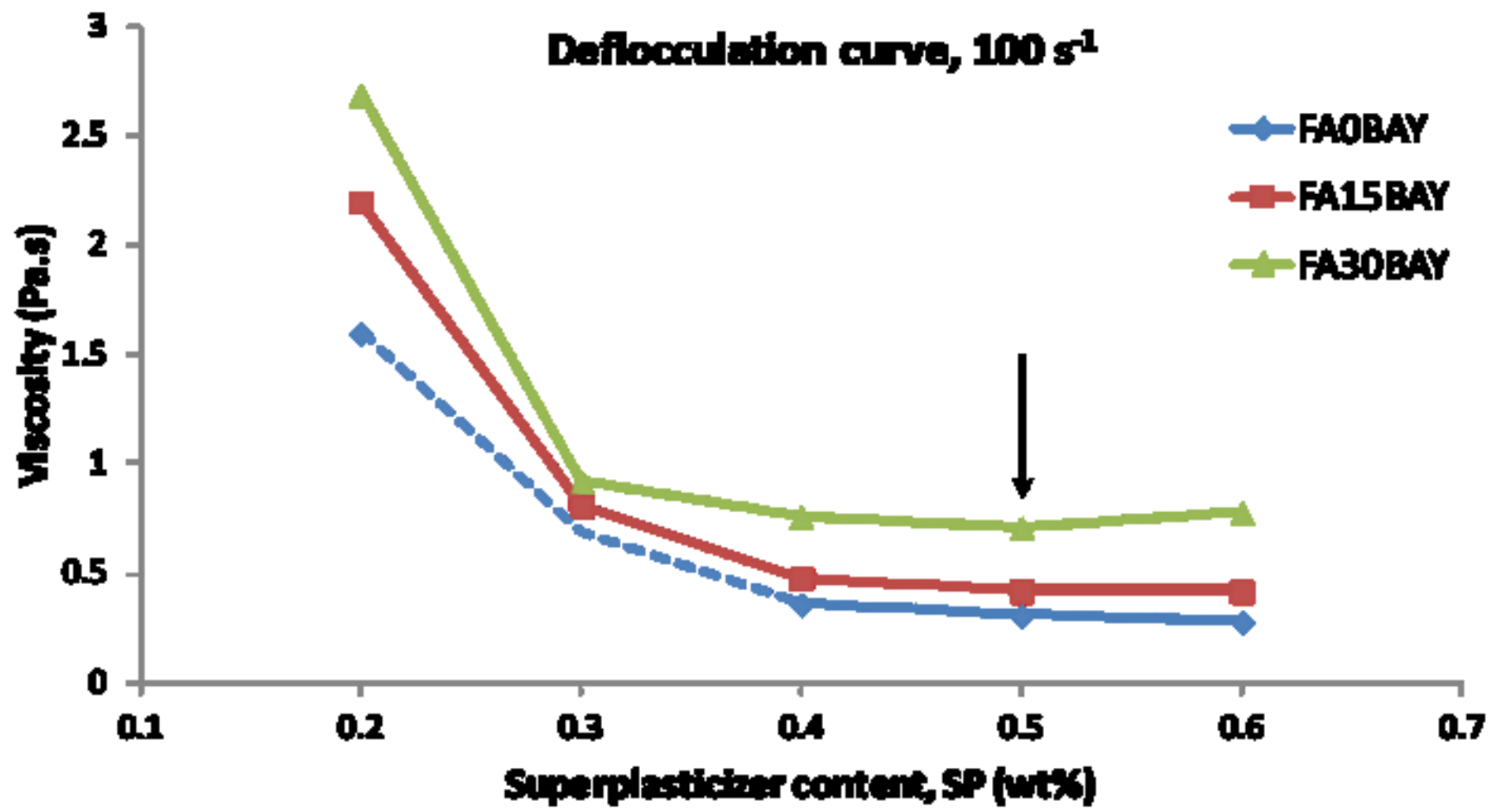
**Table 1.** RQPA results, in wt%, of the anhydrous BAY cement (FA0BAY) and fly ash powders

**Table 2.** RQPA results (wt%) of cement pastes, as a function of hydration time, obtained from LXRPD for FA#BAY pastes (w/c=0.40).

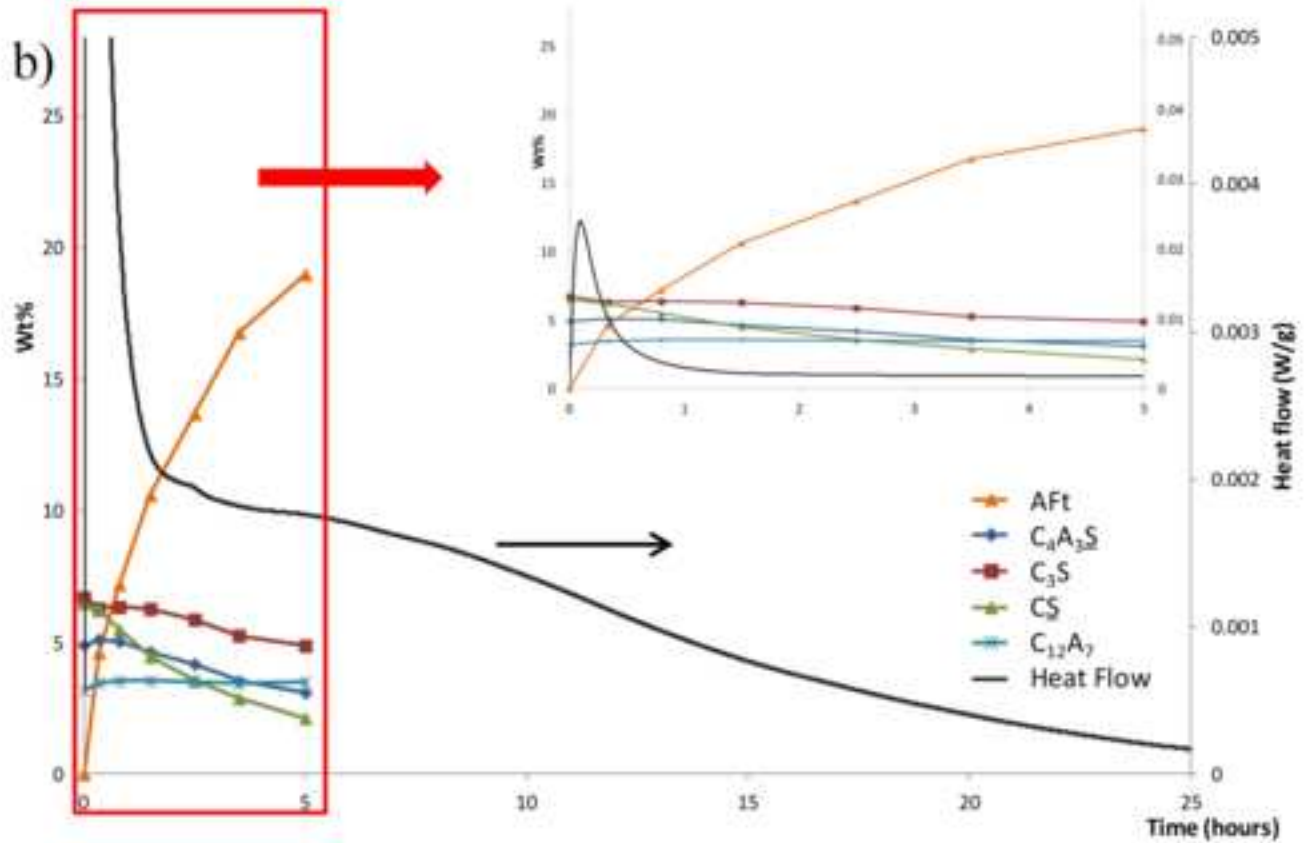
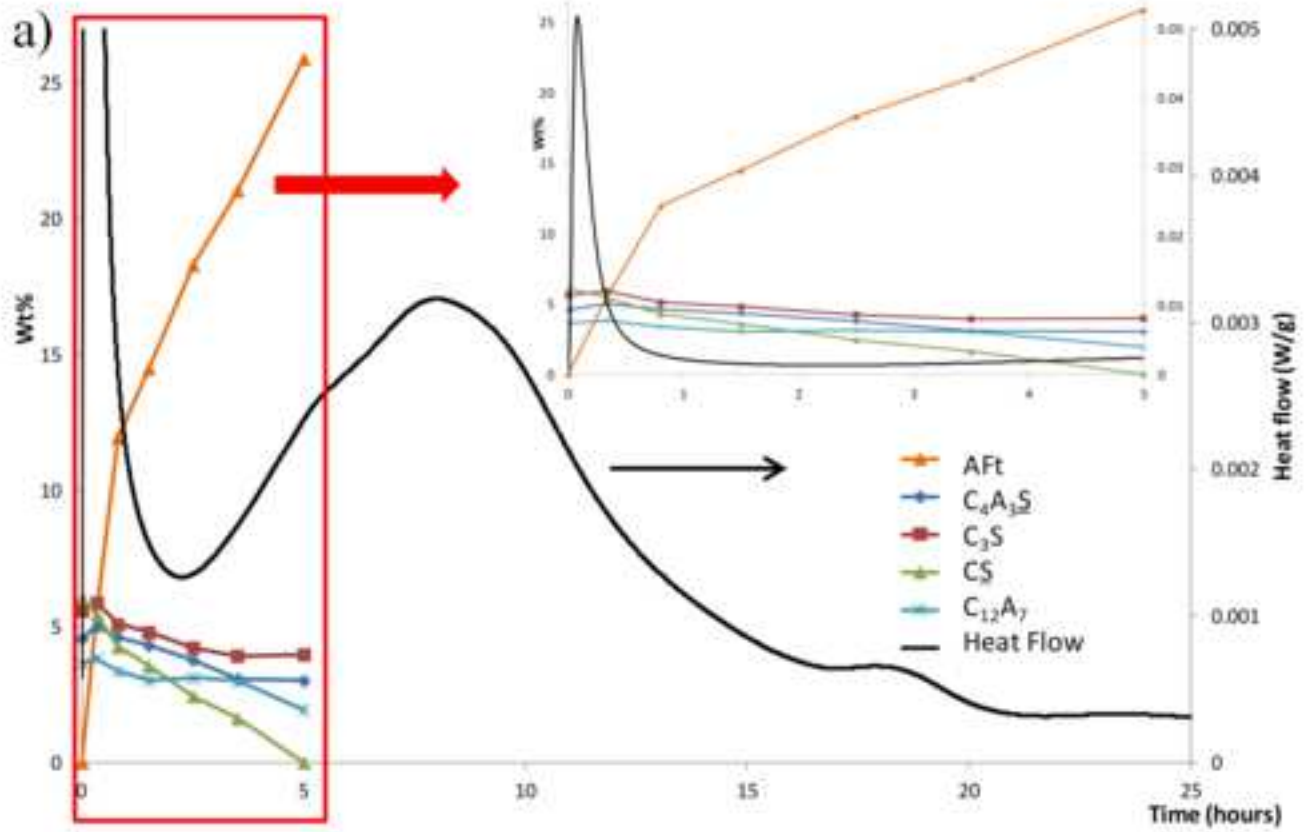
**Table 3.** RQPA comparative results (wt%), obtained from LXRPD, of FA0BAY and FA30BAY cement pastes prepared (w/c= 0.57), as a function of the hydration time.

**Table 4.** Increase of the strength (in percentage) referred to FA0BAY at the same ages.

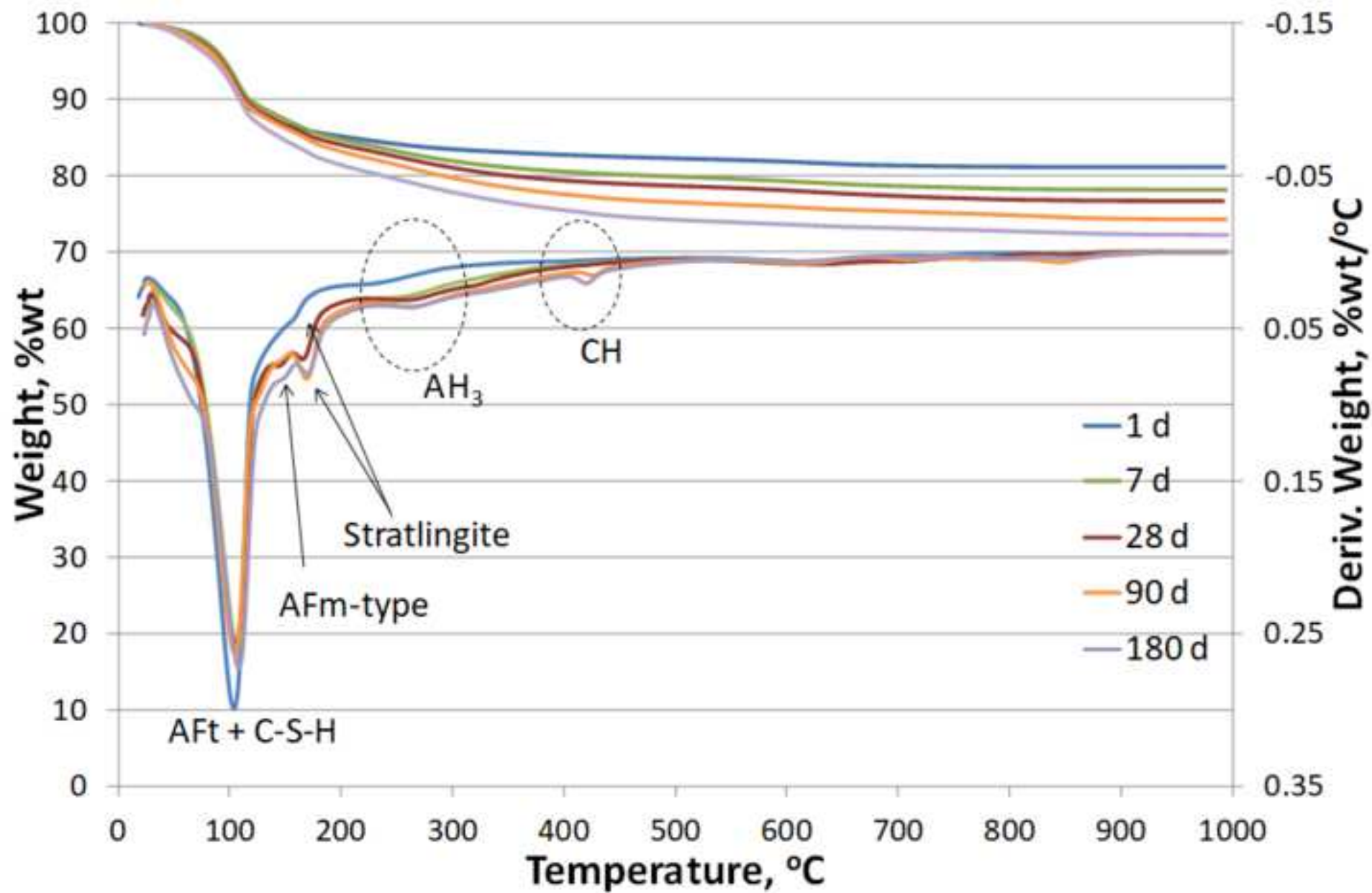
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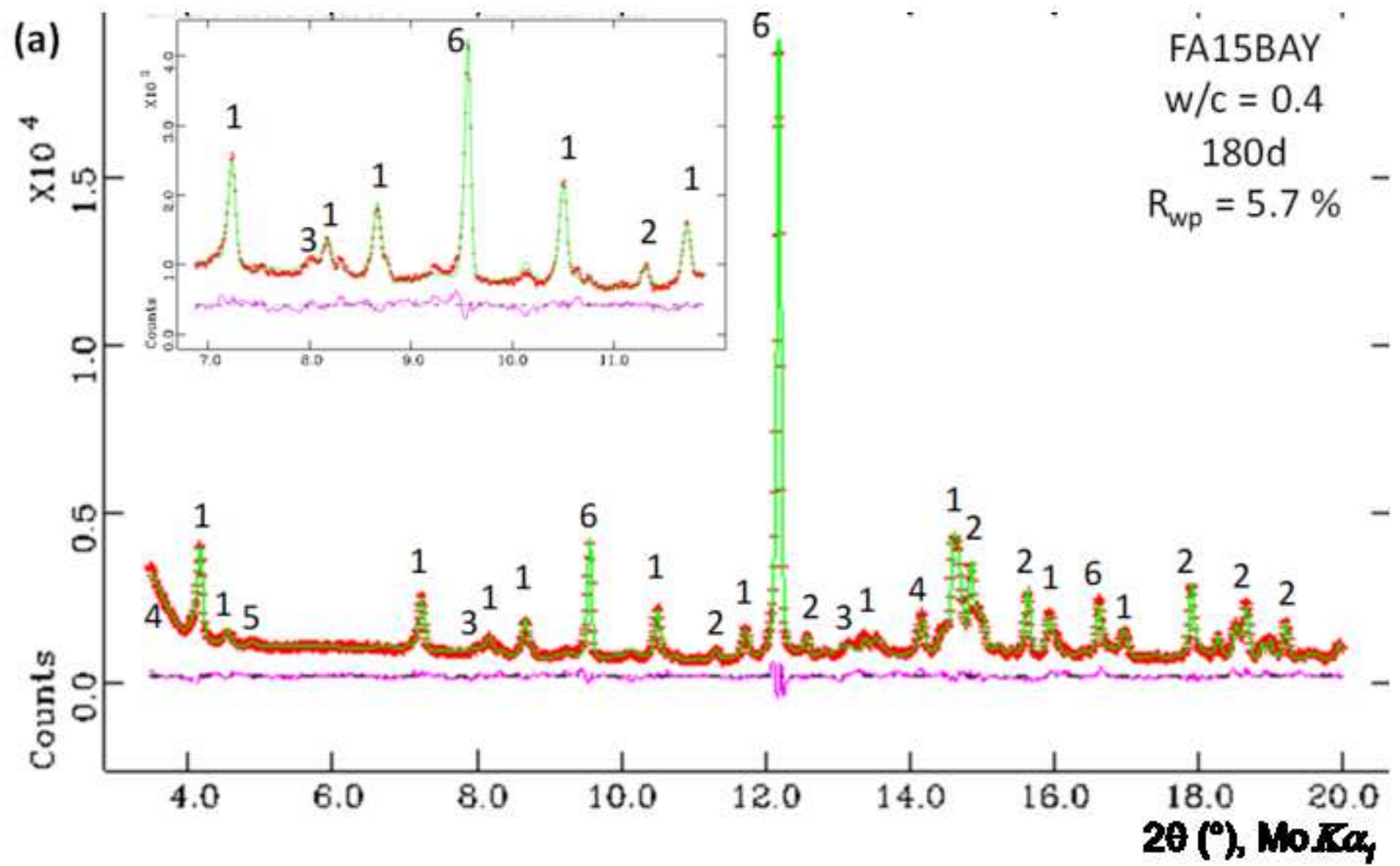
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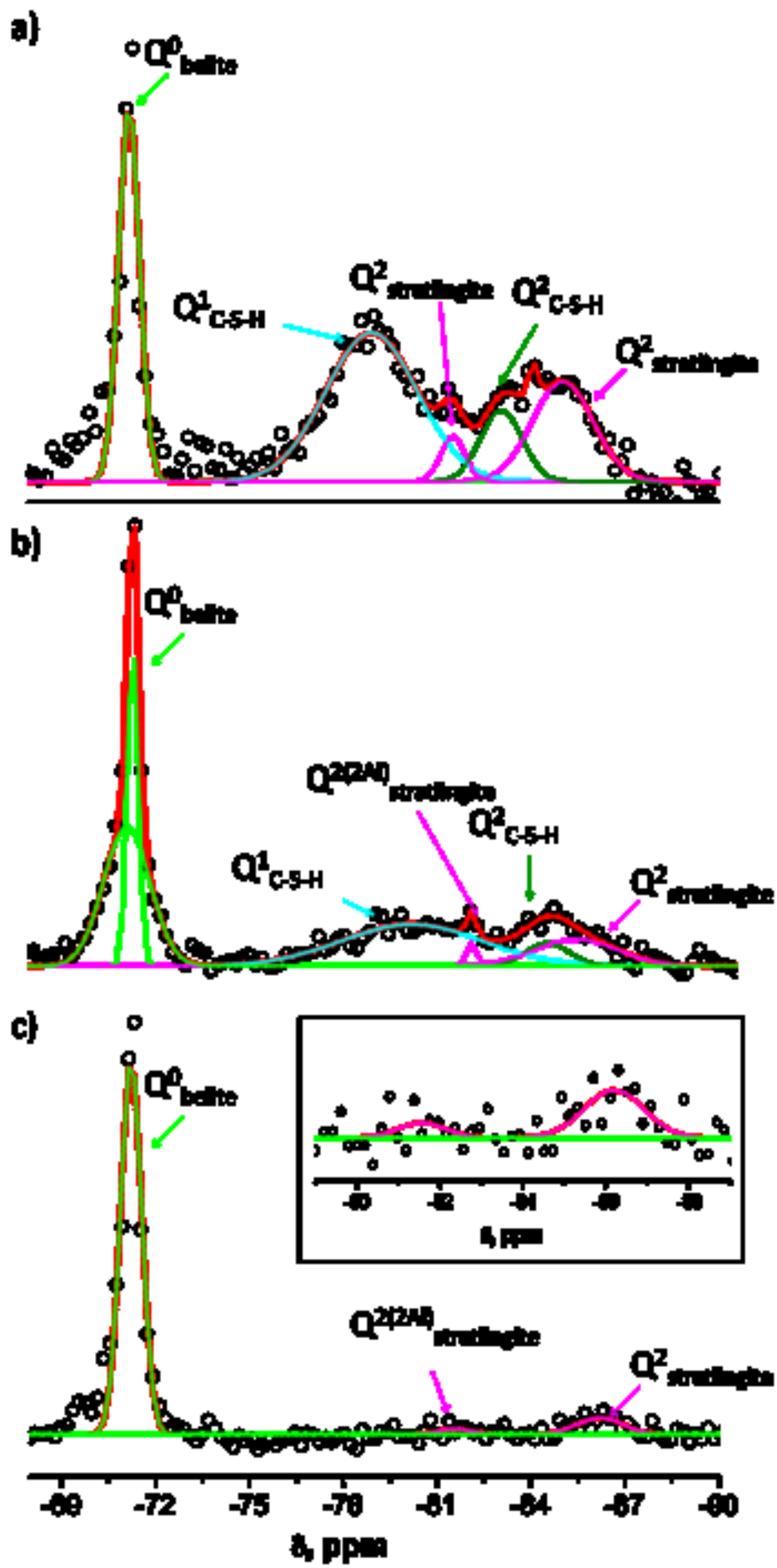
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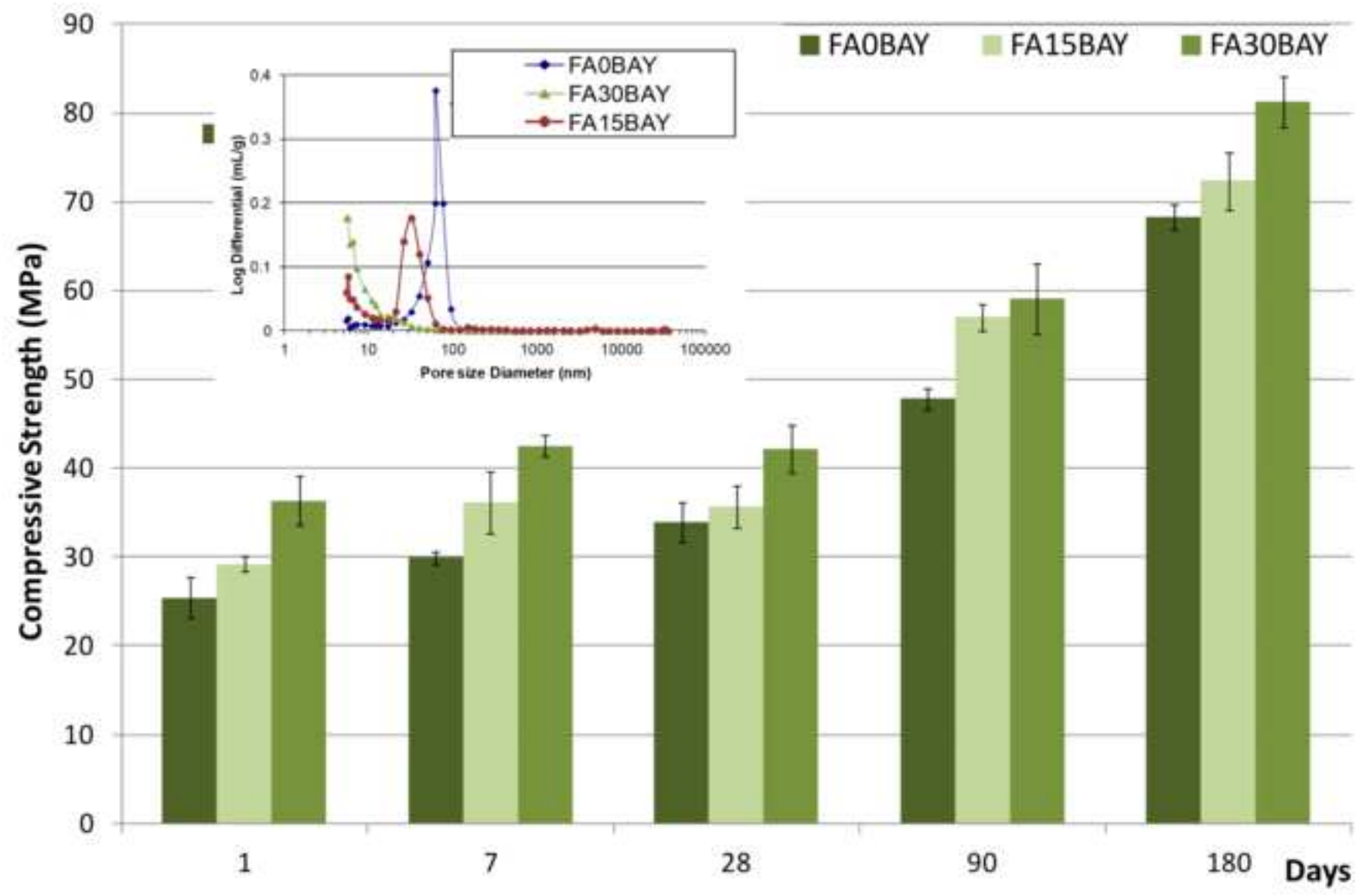






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## Tables

## Influence of Fly Ash blending on hydration and physical behavior of Belite-Alite-Ye'elimate cements

Londono-Zuluaga, D.<sup>1,2</sup>, Tobón, J.I.<sup>2</sup>, Aranda, M.A.G.<sup>1,3</sup>, Santacruz, I.<sup>1</sup>, De la Torre, A.G.<sup>\*,1</sup>

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**Table 1.** RQPA results, in wt%, of anhydrous BAY cement (FA0BAY) and fly ash powders

FA0BAY cement		Fly Ash	
$\beta$ -C <sub>2</sub> S	41.3(2)	Mullite	10.9(2)
$\gamma$ -C <sub>2</sub> S	1.1(1)	Hematite	0.5(1)
C <sub>4</sub> AF	3.6(2)	Quartz	4.6(3)
C $\bar{5}$	9.3(2)	Lime	0.2(2)
o-C <sub>4</sub> A <sub>3</sub> $\bar{5}$	7.0(2)	Periclase	0.2(1)
C <sub>3</sub> S	9.6(1)	MagnesioFerrite	1.2(2)
C <sub>12</sub> A <sub>7</sub>	5.4(1)		
F-ellestadite	3.1(1)		
ACn	19.6(2)	ACn	82.3(3)

**Table 2.** RQPA results (wt%) on cement pastes, as a function of hydration time obtained from LXRPD for FA#BAY pastes (w/c=0.4).

Phases	FA0BAY <sup>a</sup>						FA15BAY						FA30BAY					
	t <sub>0</sub>	1d	7d	28d	90d	180d	t <sub>0</sub>	1d	7d	28d	90d	180d	t <sub>0</sub>	1d	7d	28d	90d	180d
<b>C<sub>4</sub>A<sub>3</sub>S̄</b>	5.1(1)	1.3(1)	-	-	-	-	5.3(1)	2.4(1)	-	-	-	-	4.3(1)	1.0(1)	-	-	-	-
<b>γ-C<sub>2</sub>S</b>	1.2(1)	1.3(1)	1.3(1)	1.3(1)	1.1(1)	1.0(1)	1.5(2)	1.4(1)	1.3(1)	1.4(1)	0.8(1)	0.8(1)	1.4(1)	1.1(1)	1.2(1)	1.3(1)	0.8(1)	1.1(1)
<b>β-C<sub>2</sub>S</b>	32.3(1)	32.9(1)	32.4(1)	27.9(1)	16.5(2)	14.4(3)	25.0(2)	28.6(2)	28.1(2)	27.2(2)	20.3(2)	18.6(2)	19.8(2)	23.2(2)	23.2(2)	21.5(2)	19.8(2)	19.8(2)
<b>C<sub>3</sub>S</b>	7.9(2)	3.0(2)	1.0(1)	-	-	-	7.4(3)	2.4(2)	-	-	-	-	6.0(2)	1.5(1)	-	-	-	-
<b>C<sub>12</sub>A<sub>7</sub></b>	4.3(1)	2.0(1)	-	-	-	-	3.6(1)	1.9(1)	-	-	-	-	2.7(1)	1.6(1)	-	-	-	-
<b>F-ellestadite</b>	2.2(1)	3.0(2)	2.7(1)	2.3(1)	3.2(3)	3.0(3)	3.4(3)	3.4(2)	2.3(2)	2.5(1)	2.6(1)	2.1(1)	3.1(3)	2.3(1)	2.0(1)	2.1(1)	2.3(2)	2.2(2)
<b>C<sub>4</sub>AF</b>	3.3(1)	2.6(1)	-	-	-	-	2.6(1)	2.7(1)	0.2(1)	-	-	-	2.1(1)	1.6(1)	-	-	-	-
<b>C<math>\bar{S}</math></b>	7.1(1)	-	-	-	-	-	5.6(1)	-	-	-	-	-	4.7(2)	-	-	-	-	-
<b>Mullite</b>	-	-	-	-	-	-	0.5(1)	0.5(1)	1.0(1)	1.0(1)	2.1(1)	2.1(1)	1.9(2)	2.1(2)	2.4(2)	2.1(1)	2.3(1)	1.6(1)
<b>Quartz</b>	-	-	-	-	-	-	0.4(1)	0.4(1)	0.4(1)	0.4(1)	0.4(1)	0.4(1)	0.6(1)	0.7(1)	0.7(1)	0.7(1)	0.7(1)	0.7(1)
<b>C-S-H<sup>b</sup></b>	-	-	1.0(1)	1.0(1)	1.4(1)	1.1(1)	-	-	0.4(1)	1.4(1)	7.0(3)	6.7(3)	-	-	-	1.0(1)	2.1(1)	3.4(1)
<b>AFm</b>	-	-	2.4(1)	3.0(1)	5.0(1)	5.3(1)	-	-	1.2(1)	1.2(1)	1.6(1)	0.6(1)	-	-	1.8(1)	1.3(1)	0.9(1)	0.3(1)
<b>AFt</b>	-	19.5(1)	16.4(1)	16.6(1)	12.5(2)	12.7(3)	-	17.5(1)	15.3(1)	15.0(1)	15.4(2)	15.2(2)	-	14.9(2)	13.9(1)	13.4(1)	13.3(2)	13.4(2)
<b>Katoite</b>	-	-	4.0(2)	7.1(2)	4.1(2)	3.2(2)	-	-	2.8(2)	4.0(2)	4.8(2)	5.5(2)	-	-	2.6(2)	2.2(3)	3.1(3)	2.7(2)
<b>Stratlingite</b>	-	2.1(2)	5.4(3)	6.3(3)	6.4(3)	9.2(7)	-	-	4.8(4)	6.5(4)	6.6(4)	7.3(2)	-	-	1.7(1)	1.9(2)	2.8(2)	2.8(2)
<b>ACn</b>	8.1	19.7	23.6	26.2	45.4	48.2	19.3	27.5	33.8	32.4	32.5	38.8	31.3	40.9	43.9	47.0	47.7	49.4
<b>FW</b>	28.6	12.6	9.7	8.3	5.9	2.9	25.4	11.3	8.5	7.0	5.2	2.2	21.9	9.1	6.7	5.4	4.3	2.7

a. Also contains 0.1 and 0.3 wt% of CH at 90 and 180 days respectively.

b. C-S-H as clinotobermorite.

**Table 3.** RQPA comparative results (wt%) on cement pastes of FA0BAY and FA30BAY prepared at w/c of 0.57, as a function of hydration time obtained from LXRPD.

Phases	FA0BAY			FA30BAY		
	w/c 0.57			w/c 0.57		
	t <sub>0</sub>	28d	90d	t <sub>0</sub>	28d	90d
<b>C<sub>4</sub>A<sub>3</sub>S̄</b>	4.5(1)	-	-	4.0(1)	-	-
<b>γ-C<sub>2</sub>S</b>	1.1(1)	1.9(2)	1.4(2)	1.2(1)	1.1(1)	1.1(1)
<b>β-C<sub>2</sub>S</b>	28.8(1)	28.4(2)	16.5(2)	18.1(2)	18.3(2)	18.1(2)
<b>C<sub>3</sub>S</b>	7.1(2)	-	-	5.5(2)	-	-
<b>C<sub>12</sub>A<sub>7</sub></b>	3.8(1)	-	-	2.5(1)	-	-
<b>F-ellestadite</b>	2.0(1)	2.5(2)	2.4(2)	2.9(1)	1.4(2)	1.5(2)
<b>C<sub>4</sub>AF</b>	2.9(1)	-	-	2.0(1)	-	-
<b>C<sub>5</sub>S̄</b>	6.3(1)	-	-	4.3(2)	-	-
<b>Mullite</b>	-	-	-	1.8(1)	2.5(1)	2.2(1)
<b>Quartz</b>	-	-	-	0.6(1)	0.7(1)	0.7(1)
<b>C-S-H<sup>b</sup></b>	-	1.4(1)	3.6(1)	-	5.1(1)	3.0(1)
<b>AFm</b>	-	5.7(1)	5.6(1)	-	3.4(1)	4.6(1)
<b>AFt</b>	-	24.0(2)	12.7(3)	-	15.4(2)	15.0(2)
<b>Katoite</b>	-	-	-	-	-	-
<b>Stratlingite</b>	-	7.5(3)	9.5(4)	-	2.2(2)	2.0(2)
<b>ACn</b>	7.2	12.0	22.4	28.7	36.5	40.6
<b>FW</b>	36.3	16.6	15.1	28.5	13.6	11.2

a. Also contains 0.1 and 0.3 wt% of CH at 90 and 180 days respectively.

b. C-S-H as clinotobermorite.

**Table 4.** Increase of the strength (in percentage) referred to FA0BAY at the same age.

Mortar	Curing age, days				
	1	7	28	90	180
FA15BAY	15	21	5	19	6
FA30BAY	43	42	24	24	19

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*Electronic Supplementary Material*

**Influence of Fly Ash blending on hydration and physical behavior of Belite-Alite-  
Ye'elimité cements**

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This supplementary information includes:

**Table S1.** Total heat (J/g) determined by isothermal calorimetry at 5 and 24 hours for all the cement pastes prepared without and with SP.

**Figure S1.** Particle size distribution (PSD) of FA0BAY, FA15BAY, FA30BAY and FA powders.  $D_{v50}$  and  $D_{v90}$  values are given in the inset.

**Figure S2.** Flow curves of (a) FA0BAY, (b) FA15BAY and (c) FA30BAY pastes prepared at  $w/c = 0.40$  with different superplasticizer contents.

**Figure S3.** Thermogravimetric and differential thermogravimetric analyses (TGA-DTG) of (a) FA15BAY and (b) F30BAY pastes prepared with  $w/c = 0.40$ , and 0.5 wt% of superplasticizer.

**Figure S4.**  $^{27}\text{Al}$  (left) and  $^{29}\text{Si}$  (right) NMR of FA#BAY at a) 7 days, b) 90 days and c) 180 days. FA0BAY in green line (top), FA15BAY in blue line (middle) and FA30BAY in red line (bottom).

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**Table S1.** Total heat (J/g) determined by isothermal calorimetry at 5 and 24 hours for all the cement pastes prepared without and with SP.

<b>Cement Paste</b>	<b>Total heat (J/g) without SP</b>		<b>Total heat (J/g) with 0.5 wt% SP</b>	
	<i>5h</i>	<i>24h</i>	<i>5h</i>	<i>24h</i>
FA0BAY	65.5	160.8	60.5	122.2
FA15BAY	117.3	150.4	97.3	136.2
FA30BAY	100.0	129.6	86.0	112.2

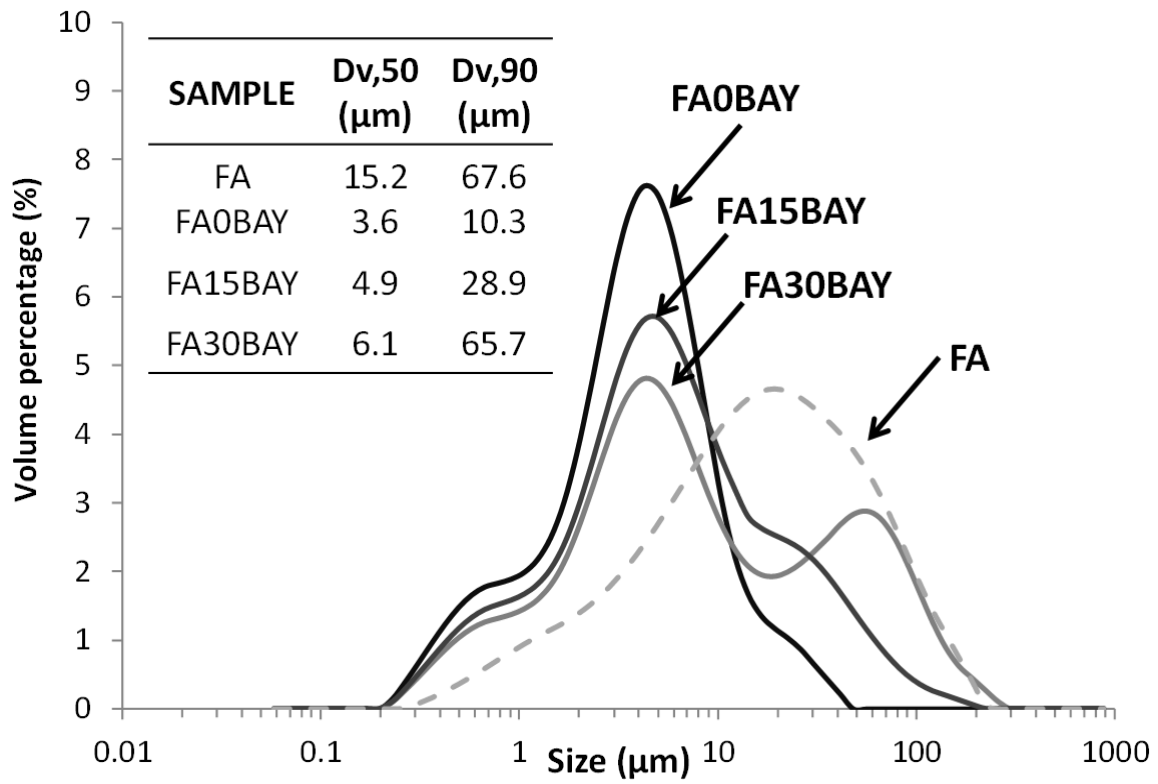


Figure S1. Particle size distribution (PSD) of FA0BAY, FA15BAY, FA30BAY and FA powders.  $D_{v50}$  and  $D_{v90}$  values are given in the inset.



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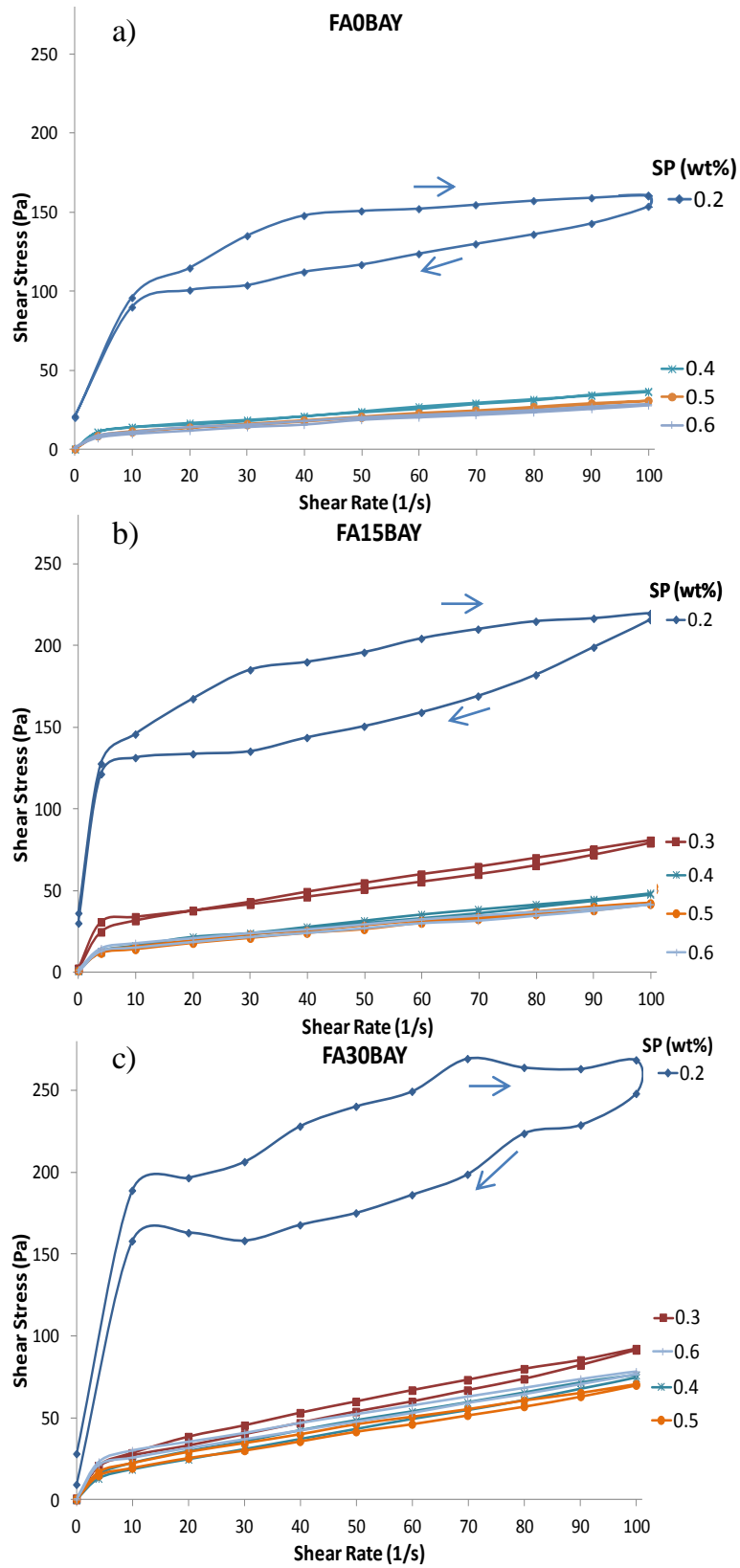


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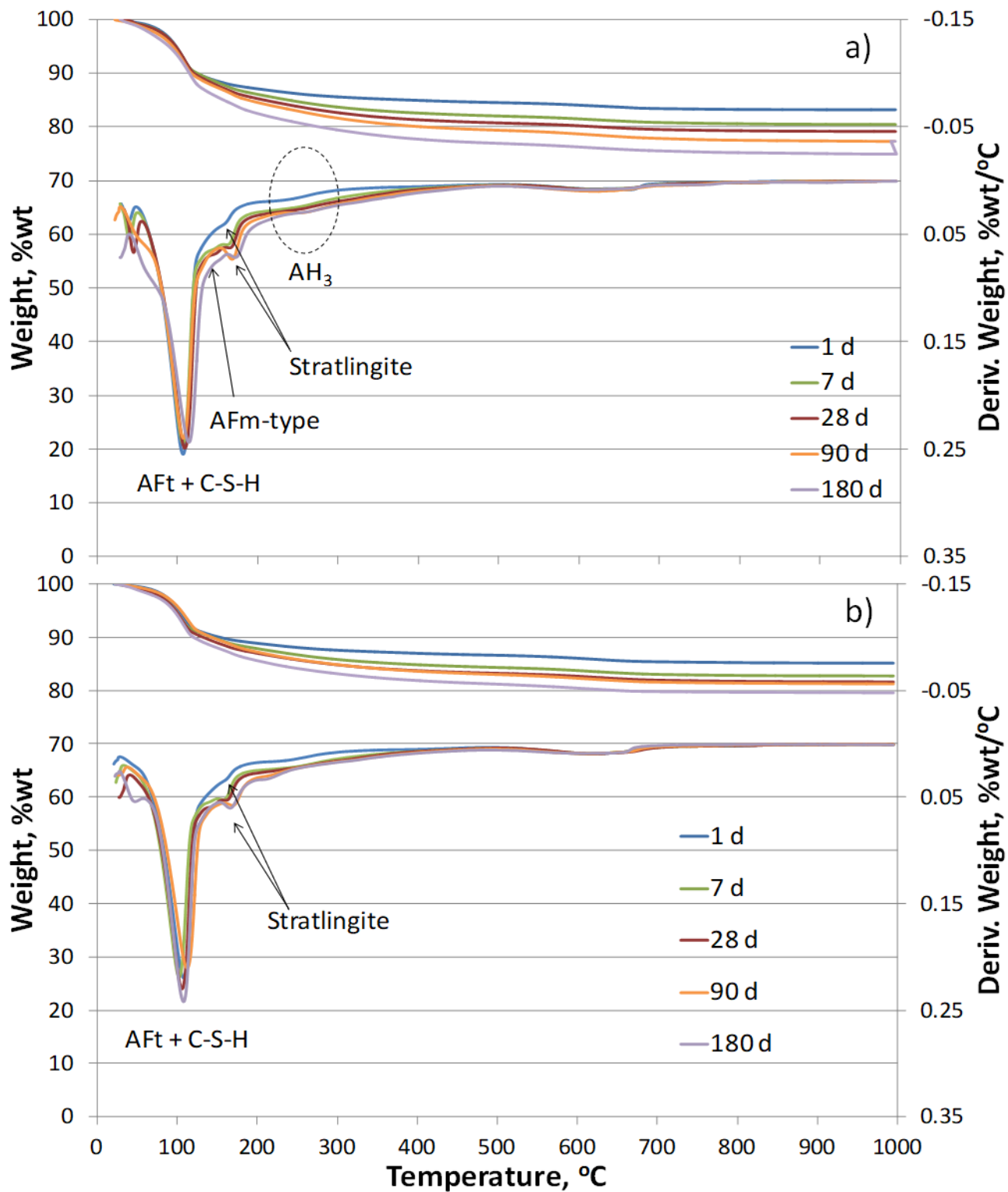


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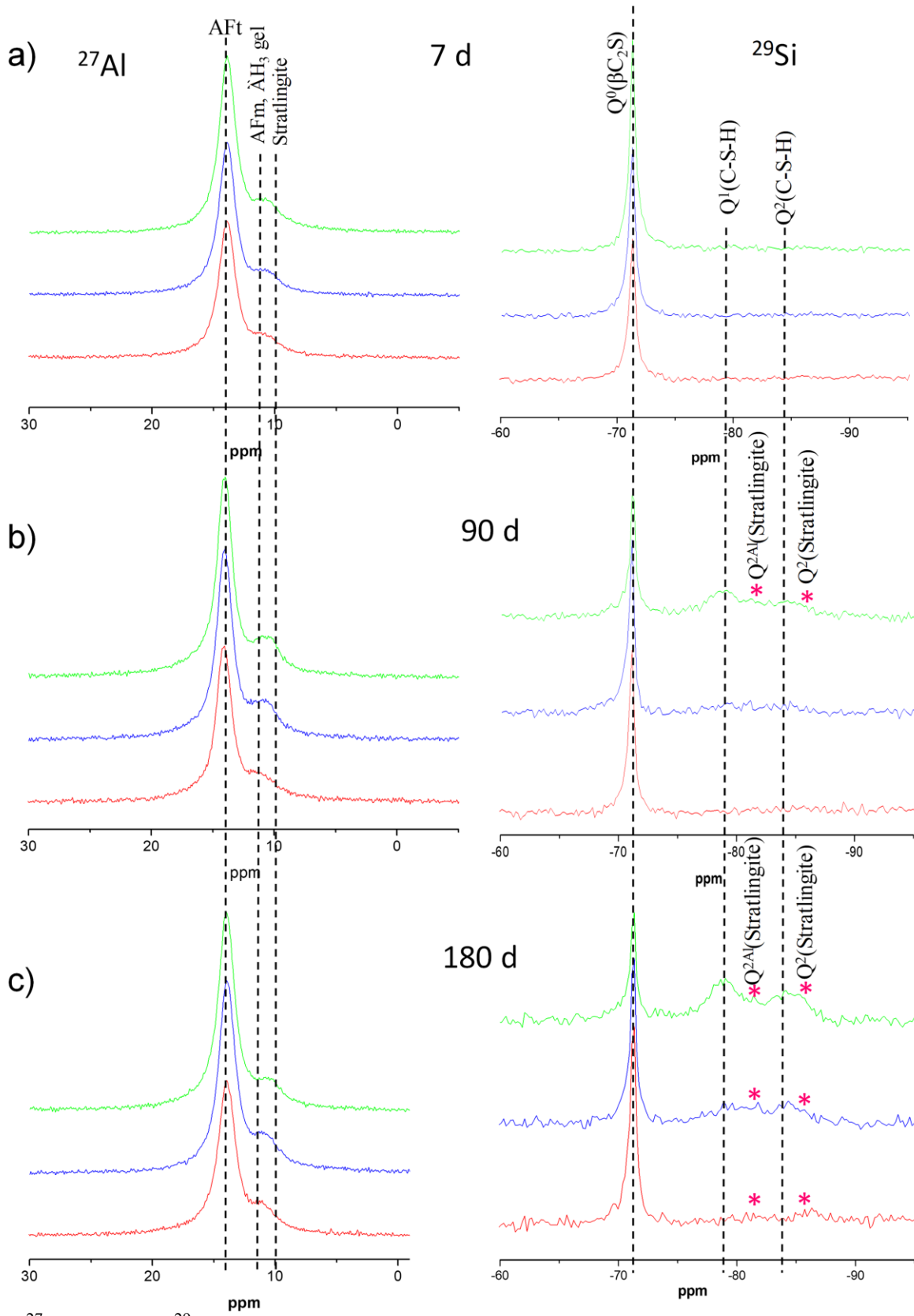


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