Hydrating Behaviour of Activated Belite Sulfoaluminate Cements

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ABSTRACT.
Belite sulfoaluminate (BSA) cements are an alternative to deplete up to 35% CO₂ emissions, comparing to the Ordinary Portland Cements (OPCs) production process. However, hydration reactivity of belite phase is slow which leads to low mechanical strengths at medium ages.

In this work, we will present some details about the hydrating behaviour of BSA cements. We have prepared BSA clinkers with nominal mineralogical composition of C₂S (50 wt%), C₄A₃S (30 wt%) and C₄AF (20 wt%). In order to enhance their hydraulic reactivity, these clinkers have been doped with borax (0.0, 1.0 and 2.0 wt% expressed as B₂O₃) to promote stabilization of α-forms of C₂S which were expected to be more reactive. The Rietveld quantitative phase analyses indicate that BSA clinker without borax has all belite as β-polymorph; the clinker with 1 wt% borax has 47% as β- and 53% as α-, and finally, the clinker with 2 wt% borax has all belite as α-polymorph. These clinkers have been mixed with gypsum to prepare cement pastes for the hydration study.

We report calorimetric data for all the cements with a w/c ratio of 0.5 and up to 6 days. The total heat evolved during early age hydration is useful information to have insights about the performances of the cements and to decide the optimum amount of gypsum to be added. These data are supported by an optical and environmental scanning electron microscopy (OM and E-SEM) study. We will correlate the morphology and amount of hydrated phases with specific signals in the calorimetric curves.

Moreover, we will present Rietveld quantitative phase analyses of pastes hydrated during 1, 3 and 6 months to better characterize the hydraulic behaviour of these cements at later ages.

Originality
The hydrating behaviour of laboratory activated belite sulfoaluminate cements is studied in detail, combining calorimetric studies, optical and environmental scanning electron microscopy. The later age hydration is followed by X-ray powder diffraction. So far, BSA cements have been studied but the merit of this approach is to differentiate the hydrating behaviour between different degrees of activation with state-of-the-art analytical tools.

Chief contributions
We will correlate heat evolved during hydration of BSA cements with morphology and amount of hydrated phases. The main goal of this study will be the demonstration of α-forms of C₂S being more reactive than β-C₂S by Rietveld quantitative phase analysis of the cement pastes. This behaviour has been previously proposed but not directly demonstrated.

Keywords: Sulfo belite cements, α-C₂S, hydration, Rietveld quantitative phase analysis.

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1. Introduction

The key component of common concrete is ordinary Portland cement (OPC). However, for one ton of OPC produced ~0.97 tons of CO₂ are released into atmosphere: 0.54 tons of CO₂ from decomposition of calcite in the kilns, and on average, 0.34 and 0.09 tons of CO₂ from the burning of the fuel and electricity for the milling, respectively. OPC production accounts for 6% of anthropogenic CO₂ emissions (Damtoft, 2008, Gartner, 2004). Belite sulfoaluminate (BSA) cements are considered as environmentally friendly cementitious materials due to the depletion of CO₂ emissions on their manufacture production, i.e. part of the calcium carbonate is replaced by calcium sulfate in order to obtain Klein’s compound or ye’elimite, achieving a reduction of ~0.19 tons of CO₂ per ton of BSA produced. In addition, these materials require lower operating temperature of the kilns, ~1250ºC and they are easily ground due to their higher porosity (Quillin, 2001). These two facts may cause a reduction of 0.04 and 0.02 tons of CO₂ per ton of BSA produced, respectively. Therefore, up to 35% CO₂ emission reduction (depending on the composition) can be attained when comparing BSA to OPC cement production. BSA cements have been already developed in China containing ye’elimite (C₄A₃S), belite (C₂S) and ferrite (C₄AF) (Glasser and Zhang, 2001; Adolfsson et al., 2007). Hereafter, cement nomenclature will be used: C=CaO, S=SiO₂, A=Al₂O₃, F=Fe₂O₃, S=SO₃ and H=H₂O. Cements made from BSA clinkers generally give high mechanical strengths at early ages (one or two days after hydration) due to the high reactivity of C₄A₃S, which shortens the dormant period (Winnefeld & Barlag, 2009). However, C₂S hydration is slow and this is the main phase.

On the other hand, it has been shown that certain minor elements enhance C₂S reactivity by stabilizing high temperature α-forms of belite at room temperature (Morsli et al., 2007a,b; Cuberos et al., 2010). Recently, active BSA cements have been patented by Lafarge (Li and Gartner, 2006) with ~30 wt% of Klein’s compound which developed mechanical strengths comparable to those of OPC, likely due to the α-forms stabilization by the addition of minor elements, f.i. boron. Furthermore, these iron-rich BSA cements have some other properties such as rapid hardening, good durability, self-stressing and volume stability, depending on the amount of gypsum added (Pera, 2004).

The main aim of this study is to quantitatively demonstrate that α-forms of C₂S hydrate much faster than the β-C₂S polymorph. The hydration processes of BSA cements, mixed with ZnO as standard, have been studied by Laboratory X-Ray Powder Diffraction [LXRPD], Rietveld methodology and chemical constraints. Calorimetric and electron microscopic studies will be also reported and discussed.

2. Experimental section

2.1. Clinkering

Three clinkers were prepared by mixing appropriated amounts of Kaolin (Aldrich), γ-Al₂O₃ (99.997% AlfaAesar), calcium carbonate (99.95-100.05% AlfaAesar), Fe₂O₃ (99.945% AlfaAesar), pure gypsum and Na₂B₄O₇·10H₂O (Aldrich). Table 1 shows elemental composition of the raw mixtures, excluding CO₂ and water, it also includes the clinker nomenclature used in this work. The three clinkers have the following theoretical phase content: 50 wt% of C₂S, 30 wt% of C₄A₃S and 20 wt% of C₄AF. The clinkering procedure was carried out as reported by Cuberos et al. (2010).

Table 1: Nominal elemental composition of raw mixtures (expressed as oxides in wt%) of BSA clinkers, excluding H₂O and CO₂.

<table>
<thead>
<tr>
<th></th>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>SO₃</th>
<th>B₂O₃</th>
<th>Na₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe_BSA_B0</td>
<td>52.7</td>
<td>17.5</td>
<td>19.2</td>
<td>6.6</td>
<td>4.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Fe_BSA_B1</td>
<td>52.0</td>
<td>17.2</td>
<td>18.9</td>
<td>6.5</td>
<td>3.9</td>
<td>1.0</td>
<td>0.5</td>
</tr>
<tr>
<td>Fe_BSA_B2</td>
<td>51.3</td>
<td>17.0</td>
<td>18.6</td>
<td>6.4</td>
<td>3.8</td>
<td>2.0</td>
<td>0.9</td>
</tr>
</tbody>
</table>
2.2. Cement preparation and hydration

Cements were prepared by mixing the laboratory prepared clinkers with 10 wt% of pure gypsum. All the cements were milled to Blaine fineness between 400 and 550 m$^2$/kg. The three cements were mixed with 25.0 wt% of ZnO (Panreac 99.95-100.05%). These mixtures, cement and standard, were hydrated with water in w/c ratio of 0.5, placed over a plastic sample holder cover with kapton foils and stored during one/three/six month(s) within a climate chamber under 100% of humidity. After the given time, LXRPD of the ground hydrated pastes were collected, without stopping the hydrating reactions.

2.3. X-Ray Powder diffraction data collection and analysis

LXRPD data were recorded on an X’Pert MPD PRO diffractometer (PANalytical) using strictly monochromatic CuK$_\alpha_1$ radiation ($\lambda=1.54059\text{Å}$) [Ge (111) primary monochromator] and X'Celerator detector. Data for each sample were collected from 10° to 70° ($2\theta$) during ~2 hours. The samples were rotated during data collection at 16 rpm in order to enhance particle statistics. All the patterns of anhydrous clinkers were analysed by the Rietveld method by using X’Pert Highscore Plus software from PANalytical B.V., version 2.2d and hydrated mixtures of cements were analyzed as implemented in the GSAS software package (Larson and Von Dreele, 1994).

2.4. Isothermal calorimetric study

The isothermal calorimetric study was performed in an eight channel home-made instrument (Halle University) using glass ampoules. Pastes were prepared with w/c ratio of 0.5, and the heat flow was collected up to 144 h at 20ºC.

2.5. Cryo Scanning Electron Microscopy (cryo-SEM)

Pieces of cement pastes were measured using a LEO 1530 VP Gemini microscope coupled with an energy dispersive X-ray (EDX) analyzer. Pastes are cryogenized by liquid nitrogen (-190ºC) and kept at that temperature during imaging.

3. Results and discussion

3.1. Laboratory Clinkers

Table 2 shows Rietveld quantitative phase analysis (RQPA) for the three clinkers, including derived amorphous (non-diffracting) contents calculated by adding ZnO as an internal standard (De la Torre et al., 2001). Free lime was not observed revealing that the clinkering process is finished at 1300ºC, which is 150ºC lower than that used for fabrication of ordinary Portland clinkers. The percentages of main phases (C$_2$S and C$_4$A$_3$S) are quite close to the targeted values, 50 and 30 wt%, respectively. Furthermore, the activation has been achieved by adding B and Na, as different amounts of $\alpha''$-H-C$_2$S have been stabilized in Fe_BSA_B1 and Fe_BSA_B2.

Two mechanisms are known for the chemical activation of low-reacting phase(s): firstly, the stabilization at room temperature of high temperature polymorph(s). This is proved by the data reported in Table 2. Secondly, chemical doping within a given phase, leading to larger unit cell volumes, may also increase the reactivity for a given polymorph. This has been studied, and proved to take place, in the borax activation of belite sulfoaluminate clinkers. The refined unit cell value of $\alpha''$-H-C$_2$S in Fe_BSA_B2 was 354.7 Å$^3$ which is much bigger than the reported value for the stoichiometric phase, 347.5 Å$^3$. However, the unit cell volume of $\alpha''$-H-C$_2$S in Fe_BSA_B1, 346.7 Å$^3$, is very similar to that previously given. On the other hand, increasing amounts of activators (B and Na) have promoted the formation of amorphous/non-diffracting phases, as expected, see Table 2, due to their influence on melting temperatures and viscosity of melted phase(s). Moreover, the percentage of crystalline C$_4$AF decreases as
the amount of activators increases. Thus, it can be speculated that these amorphous phases are Al-Fe rich. In addition to that, the possible incorporation of the activators within this phase may be indirectly estimated from the evolution of the unit cell volumes of this phase for the three compositions. The measured unit cell volumes are 429.3(1), 433.2(1) and 434.0(1) Å³ for Fe_BSA_B0, Fe_BSA_B1 and Fe_BSA_B2, respectively. The small, but measurable, unit cell volume increase indicates doping of the activators. However, a detailed study is needed to establish the effect of B and Na in the crystal structure of C₄AF within this type of clinkers.

Table 2: Quantitative phase analysis results (wt%) for the clinkers obtained at 1300ºC for 15 min determined by Rietveld methodology, including amorphous/non-diffracting contents.

<table>
<thead>
<tr>
<th>Phases</th>
<th>Fe_BSA_B0</th>
<th>Fe_BSA_B1</th>
<th>Fe_BSA_B2</th>
</tr>
</thead>
<tbody>
<tr>
<td>α′H-C₂S</td>
<td>-</td>
<td>26.6(4)</td>
<td>46.9(4)</td>
</tr>
<tr>
<td>β-C₂S</td>
<td>52.5(3)</td>
<td>22.9(4)</td>
<td>-</td>
</tr>
<tr>
<td>C₄A₃S</td>
<td>28.0(2)</td>
<td>29.6(2)</td>
<td>29.2(2)</td>
</tr>
<tr>
<td>C₄AF</td>
<td>17.8(2)</td>
<td>14.3(2)</td>
<td>11.1(2)</td>
</tr>
<tr>
<td>C₃A</td>
<td>1.6(1)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Amorphous</td>
<td>~0.0</td>
<td>~6.7</td>
<td>~12.8</td>
</tr>
</tbody>
</table>

3.2. Cement pastes

Quantitative phase analysis of the cement pastes evolution makes sense only if the water contents are appropriated. This initial check is necessary as the ratio surface/volume of the pastes for powder diffraction experiment is high and it may lead to a drying effect which it would slow down/stop the hydration reactions (in this particular experimental setting). Therefore, the water contents after each hydration time were checked before collecting the powder diffraction data. In order to do so, a portion of every cement paste was heated up to 800ºC in a furnace, and the weight loss measured. Table 3 reports water losses (in weight percentage) after one, three and six months of hydration. Obtained values approximately match the amount of water initially added, 33.3 wt%, this number does not take into account the ZnO addition. Thus, ‘drying effect’ can be ruled out in the experimental conditions described in the previous section.

Table 3: Total water loss (wt% up to 800ºC) after each time of hydration. Free water content (wt%) calculated using Rietveld data and stoichiometric reactions. Degree of reaction, α, for overall belite phases (see text).

<table>
<thead>
<tr>
<th>Total water loss (wt%)</th>
<th>Free water (wt%)</th>
<th>Degree of reaction, α, of overall belite phases (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B0</td>
<td>B1</td>
</tr>
<tr>
<td>t₀</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>t₁month</td>
<td>38.6</td>
<td>39.2</td>
</tr>
<tr>
<td>t₃months</td>
<td>34.4</td>
<td>35.4</td>
</tr>
<tr>
<td>t₆months</td>
<td>36.0</td>
<td>37.4</td>
</tr>
</tbody>
</table>

Once water content was confirmed to be acceptably constant, cement powder patterns were analyzed. As a first step, phase identification was performed, concluding that C₄A₃S and C₄AF have disappeared after one month of hydration in all the cements. On the other hand, all powder patterns present Ca₆AS₃H₄₂ [ettringite or AFt phase], Ca₃ASH₄ [katoite] and Ca₂ASH₈ [straetlingite]. After phase identification, RQPA were performed as indicated in the experimental section. Figure 1 shows, as an example, the fits obtained for the three cement pastes after six months of hydration. Three main points characterize the hydration processes: i) disappearance of crystalline anhydrous phases; ii) appearance of both crystalline, i.e. AFt, and amorphous phases such as calcium silicate (C-S-H) and aluminate (C-A-H) hydrate gels; and iii) diminution of free water. Since RQPA results are normalized to 100 wt% of crystalline phases, the percentage of the non-reactive phases such as ZnO is not constant due to the apparition of amorphous
phases. Hence, in order to fully extract all the information about the hydration of cement pastes, direct RQPA results need to be normalized to include the amorphous phases and free water (Martín-Sedeño et al., 2010). The methodology is based on the assumption that one crystalline phase remains unreacted from one powder pattern to the next. ZnO is an inert standard and is used to infer the amounts of other phases that are reacting. Using this methodology, direct Rietveld results were normalized in order to include free water, which is also included in Table 3, and amorphous contents, such as C-S-H and C-A-H gels. Figure 2 shows normalized quantitative phase analysis for each cement paste.

The sequence of reactions during hydration for this type of cements is explained in detail next. Firstly, it must be noted that modelling the hydration of this type of cement is easier than that of aluminium-rich belite sulfoaluminate cements as only three phases are present in the clinkers. Furthermore, the hydration reactions for OPC are also more complex as at least four crystalline phases are present in the clinkers. Secondly, the most reactive phase, ye’elimite, combines with gypsum and water to form ettringite, AFt, see reaction [1]. The amount of ye’elimite in these cements is larger than the corresponding amount of gypsum added, taken into account the molar ratio given in equation 1. Therefore, the slight excess of ye’elimite reacts with water to give AFm, non-crystalline phase, see equation 2.

\[
\begin{align*}
C_4A_3S + 2C_SH_2 + 34H & \rightarrow C_6A_3S_3H_32 + 2AH_3 \\
C_4A_3S + (16+x)H & \rightarrow C_4ASH_{(10+x)} + 2AH_3 \quad (0 \leq x \leq 4)
\end{align*}
\]

Thirdly, it was observed that not only C4A3S but also C4AF have disappeared after one month of hydration. This second phase may also react with gypsum and water to form ettringite. However, with the added amount of gypsum, there is not available free gypsum. Therefore, the hydration of C4AF also yields AFm amorphous-type phase(s) according to equation 3. Fourthly, \(\alpha\)- and \(\beta\)-C2S polymorphs may react with water in three different ways, see reactions 4-6. Crystalline C2ASH8 and C3ASH4 have been quantified in this study. C1.7SH4 is an amorphous gel with the average composition taken from Scrivener et al., (2004), which has been used to derive the amorphous C-S-H gel that is appearing.

\[
\begin{align*}
C_4AF + 16H & \rightarrow 2C_2(A_{0.5}F_{0.5})H_8 \\
C_2S + AH_3 + 5H & \rightarrow C_2ASH_8 \\
5C_2S + AH_3 + 17.2H & \rightarrow 2C_3ASH_4 + 2C_{1.7}SH_4 + 0.2CH \\
C_2S + 4.3H & \rightarrow 2C_{1.7}SH_4 + 0.3CH
\end{align*}
\]

Finally, the degree of reaction, \(\alpha\), of C2S phases has been calculated using normalized data shown in Figure 2, according to the following expression [7]. Overall belite reactivities are also given in Table 3. These data quantitatively confirm the higher rate of hydration of \(\alpha'_{1T}\)-C2S, and it can be graphically observed in Figure 2. It can be inferred from these data that cements with \(\alpha'_{1T}\)-C2S will develop higher mechanical strengths from one month of hydration. A study aimed to produce larger amounts of clinkers to study both hydration reactions and strength developments is in progress.

\[
\alpha = \frac{w_{\text{phase}-n} - w_{\text{phase}-n}^0}{w_{\text{phase}-n}^0}
\]

On the other hand, Figure 3 (left) shows heat flow for C10_Fe_BSA_Bx cement pastes. The first broad signal is associated with ettringite and aluminous/iron ill crystallized (C-A-H gel) phase formation. Table 4 shows total heat evolved (J/g) at selected times. Non-active cement (C10_Fe_BSA_B0) released much more heat at 3 hours. This heat is related to AFt formation, mainly, by reaction [1] which is retarded in someway by the activators (Li et al., 2007). After one day of hydration, heat evolved by doped BSA cement pastes increase at a higher pace than undoped ones, which proves the activation of the cements.
It has to be borne in mind that some phases predicted by chemical reactions, such as AH₃ or CH, were not detected as crystalline phases. AH₃ reacts with belite to give some crystalline phases discussed above. In any case, the remaining AH₃ and a very small amount of CH were considered as ill-crystallized phases and included as C-A-H or C-S-H amorphous gels, respectively. These amorphous gels have been detected by cryo-SEM, arrow in Figure 3-right.

3. Conclusions
The main goal of this contribution is that it has been quantitatively demonstrated that \(\alpha'_1\)C₂S belite polymorph can be stabilized by borax in belite sulfoaluminate clinkers and that this polymorph hydrates much faster than \(\beta\)-C₂S polymorph.
Figure 3: (Left) Selected heat flow curves for C10_Fe_BSA_Bx. (Right) Cryo-SEM photograph of a paste after 40 minutes of hydration including EDX microanalysis of the region shown to highlight the amorphous aluminate gel.

4. References