X-ray diffraction, cements and environment, three worlds in one.

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Abstract. This keynote lecture will be focused on the strategies for reducing CO₂ emissions in the cement production. Concretely, the production of ecocements with optimised formulations that yield reductions in CO₂ emissions of up to 25%, when compared to OPC production. Phase assemblage has to be carefully optimised to be competitive and these new ecocements should develop compressive strengths of at least 50 MPa at 28 days of hydration. Optimised compositions of several ecocements will be discussed, but all of them are ye'elimite or calcium sulphoaluminate containing ones: belite-ye'elimite-ferrite (BYF), belite-alite-ye'elimite (BAY) and ye'elimite rich ones (CSA). The clinkering temperature of BYF and BAY has to be established to obtain the targeted phase assemblages. Moreover, the stabilisation of alpha-forms of belite is needed to develop high mechanical strengths at early ages. The benefits of the use of waste materials (such as fly ash or slag) as additions to ecocements are three-fold: lower CO₂ emissions due to clinker replacement; valorisation of “useless” products that need a lot of landscape and the consequent efficient consumption of raw materials; and to enhance mechanical properties of the corresponding mortars. The design of appropriate CSA, BYF and BAY mortars, with the final aim of knowing and controlling the hydration mechanisms, will be presented. Particularly, the role of i) type and amount of set regulator (gypsum, anhydrite, etc.), ii) water/cement ratio (w/c); iii) superplasticiser; and iv) pozzolanic additions will be discussed. The role of these parameters in the microstructure and hydraulic behaviour has been investigated through traditional techniques as well as advanced synchrotron characterisation. The former include laboratory/synchrotron X-ray powder diffraction combined with Rietveld methodology (to obtain phase assemblage), electron microscopy techniques for paste microstructure determination, rheological studies (to control the effect of the different additives, w/c ratio and setting time retarders) and mechanical tests (setting times, compressive strengths and dimensional stability). The latter comprise a group of techniques available at synchrotrons such as: i) high temperature x-ray diffraction for clinker studies and ii) total scattering data to be analysed by pair distribution function, PDF.

1 Introduction

Ye’elimite containing-cements are considered as eco-cements as less CO₂ is released during their production compared to OPC. This is due to the presence of ye’elimite in their composition, which is a low calcite-demanding phase (0.22 t/t phase). Other phases present in OPC such as alite (0.58 t/phase), belite (0.51 t/phase), tricalcium aluminate (0.49 t/phase) or calcium aluminate ferrite (0.22 t/phase) are high calcite-demanding phases. For this reason, and their high performances, the research on these cements has recently been increased [1]. The mineralogy of these new binders is of great importance to understand and predict final performances of the derived mortars and concretes.

Ye’elimite, also called Klein’ salt or tetracalcium trialuminate sulphate C₄A₃S, crystallizes as an orthorhombic phase [2]. Moreover, the presence of foreign ions in the structure stabilizes a pseudo-cubic form [3]. Ye’elimite-containing cements can be gathered in three main groups [1]: i) Calcium Sulpho-Aluminate (CSA), ii) Belite Calcium Sulpho-Aluminate or sulphobelite (BYF, from Belite-Ye’elimite-Ferrite cements) and iii) Belite-Alite-Ye’elimite (BAY) cements.

In the last ten years, research has been ongoing to solve the technological problem of BYF, which is the low mechanical strengths developed at early ages [4–6] by stabilising high-temperature belite polymorphs (α-forms) by the addition of minor elements. Another strategy to active these ye’elimite containing cements is the
production of a cement with both alite and belite (BAY) [7–9].

The hydration reactions involving ye'elimite have to be fully understood to control and tune-up these type of cements. There is some controversy in the literature data about the hydration behaviour of ye'elimite in absence of other soluble sulphate groups [10–12]. In addition, belite reactivity is important, especially for BYF and BAY cements. Independently on the polymorphism, the hydration behaviour of belite may yield a nanocrystalline C-S-H gel, similar to that arising from the hydration of alite. However, in hydrated BYF systems, belite coexists with a hydrated amorphous aluminate rich environment which favours the formation of an AFm-type phase called stratlingite [4,13,14], which may play an important role in mechanical strengths [15].

2 Clinkering of BYF and BAY.

2.1 Clinkering in-situ Synchrotron X-ray powder diffraction (SXRPD) study of BYF and aBYF.

Clinkering reactions of BYF and aBYF (active BYF) were studied by in-situ SXRPD. Several reactions were followed including $\alpha''_H\,C_2S \rightarrow \beta\,C_2S$ polymorphic transformation, the decomposition of ye'elimite and the melting of C4AF. Overall, these temperatures decrease with the addition of B2O3 [16]. Figure 1 shows the phase evolution, including the melted phase, for aBYF and a Rietveld plot of this clinker at 1586 K as an example. The most important results were that i) the $\alpha''_H\,\rightarrow\beta$ polymorphic transformation temperature was reduced from ~1650 K in BYF to 1250 K in aBYF; ii) the decomposition temperature of ye'elimite was also lowered from ~1550 K in BYF to ~1500 K in aBYF. Furthermore, the addition of B2O3 also decreased the melting temperature of C4AF from ~1550 K to ~1430 K.

2.2 Clinkering of BYF and BAY: Activation.

The "medium-scale" synthesis (~2 kg) of BYF and BAY clinkers was performed by mixing the same raw materials commonly used in cement plants. The targeted composition of BYF clinker was ~50 wt% of C2S, ~30 wt% of C3A1, and ~20 wt% of C4AF and that of BAY clinkers was 25-45 wt% of C2S, 30-45 wt% of C3S, ~20 wt% of C4A1, and ~5 wt% of C4AF. In the case of BAY clinkers, only CaF2 or CaF2 and ZnO (BAYZ) were added, to success in the preparation of BAY and BAYZ clinkers with the coexistence of alite and ye'elimite phases [17] by adding CaF2 and ZnO was a success.

On the one hand, it is noticeable that the addition of borax to raw mixtures has totally or partially stabilised $\alpha''_H\,C_2S$ and pseudo-cubic ye'elimite. On the other hand, the preparation and scale-up of BAY and BAYZ clinkers with the coexistence of alite and ye'elimite phases [17] by adding CaF2 and ZnO was a success.

Table 1. Mineralogical phase composition of ye'elimite containing clinkers synthetized at medium scale (~2 kg) in the laboratory.

<table>
<thead>
<tr>
<th>Phase</th>
<th>BYF</th>
<th>aBYF</th>
<th>BAY</th>
<th>BAYZ</th>
<th>aBAYZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha''_H,C_2S$</td>
<td>-</td>
<td>57(2)</td>
<td></td>
<td></td>
<td>18.1(3)</td>
</tr>
<tr>
<td>$\beta,C_2S$</td>
<td>48.7(6)</td>
<td>59.4(2)</td>
<td>28.4(3)</td>
<td>42.1(2)</td>
<td></td>
</tr>
<tr>
<td>$\gamma,C_2S$</td>
<td>2.6(5)</td>
<td>1.2(1)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C3S</td>
<td>14.3(2)</td>
<td>41.5(2)</td>
<td>15.8(2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>o-C4A1,</td>
<td>15(1)</td>
<td>10.4(1)</td>
<td>9.3(3)</td>
<td>2.9(2)</td>
<td></td>
</tr>
<tr>
<td>c-C4A1,</td>
<td>14(1)</td>
<td>31(2)</td>
<td>8.1(3)</td>
<td>4.8(2)</td>
<td></td>
</tr>
<tr>
<td>C4AF</td>
<td>14.9(2)</td>
<td>10.16(2)</td>
<td>6.5(2)</td>
<td>3.8(1)</td>
<td>3.2</td>
</tr>
<tr>
<td>Minor phases</td>
<td>5.7</td>
<td>2.1</td>
<td>5.0(1)</td>
<td>9.0(1)</td>
<td>13.1</td>
</tr>
</tbody>
</table>
3 Hydration of ye'elimite containing cements: CSA, BYF and BAY.

3.1 Role of activation of ye'elimite bearing cements.

Mortars prepared with aBYF cement developed higher compressive strengths than BYF at any hydration age and BAY at early hydration time (up to 7 days), and higher strengths than BAY at 28 d, Figure 2, independently of the type and amount of sulphate source [6,18]. Standard BYF clinker contains $\beta$-C$_2$S, as main phase and orthorhombic ye'elimite. It has been demonstrated that $\beta$-C$_2$S in these experimental conditions reacts at a higher pace than alpha forms in active BYF [6] to yield stratlingite. This behaviour may well be justified with the formation of high amounts of ettringite at early hours which implies a concomitant large quantity of amorphous aluminium hydroxide. The availability of amorphous AH$_3$ promotes the precipitation of stratlingite, C$_2$ASH$_8$, from belite reaction. In conclusion, the hydration behaviour of C$_2$S is likely more dependent on the chemical environment than on its polymorphism. However, it must be underlined that although the phases in BYF react faster than in aBYF, the standard cement develops much smaller compressive strength, Figure 2.

![Fig. 2. Compressive strengths of CSA, BYF and BAY mortars.](image)

Furthermore, the activation by synthesising clinkers with alite and ye'elimite, i.e. BAY clinkers, has been a success since BAY mortars show higher compressive strengths than BYF mortars, prepared under similar conditions (anhydrite as setting regulator and w/c) at any hydration time, Figure 2.

None of BYF or BAY cements have developed higher mechanical strengths than CSA cements, Figure 2. However, CSA cements are more expensive due to the need of high amounts of Al$_2$O$_3$, mainly as highly pure bauxite. So BYF and BAY are proposed as a suitable cheap environmental solution.

3.2 Role of type of setting regulator: gypsum, bassanite or anhydrite

The effect on hydration behaviour and mechanical strengths of three different setting regulators (gypsum, bassanite and anhydrite) has also been studied. The dissolution rate of the different studied sulphate sources is a key point to control the reactions during hydration of CSA and BYF cements, and hence the mechanical properties of the corresponding pastes and mortars. The dissolution of anhydrite is the slowest of the three sulphate sources. Cements and mortars prepared with anhydrite, showed higher initial setting times than those prepared with gypsum. Consequently, mechanical strengths after 3 days of hydration, Figure 2, are lower than those of mortars prepared with CSA or BYF with gypsum. However, these longer setting times of anhydrite pastes provides them with high plasticity to accommodate the precipitation of ettringite at later ages, and thus mortars showed similar compressive strength values Figure 2.

CSA or BYF with bassanite pastes showed high water demand, high viscosity values and short setting times with the consequent dramatic effect on the mechanical strength values of the corresponding mortars. This makes necessary the selection of a hydration retarder which also reduces the viscosity of the pastes [18,19], Figure 2.

![Fig. 3. Flow curves of CSA and aBYF pastes prepared with bassanite as setting regulator without and with (open symbols) a superplasticizer/retarder based on polycarboxylate.](image)

The effect of three additives (polycarboxylate, tartaric acid and phosphonic acid) on CSA pastes and mortars was studied [20]. The amount of each additive was optimised elsewhere [20] and all of them improved the workability of pastes, where the polycarboxylate (PC) was the best additive in reducing viscosity at very early ages. All these parameters could be controlled, making possible the design and preparation of mortars with selected properties for specific engineering applications.
4 Hydration of pure phases related to CSA, BYF and BAY.

4.1 Hydration of ye’elimite.

The crystal structures of orthohombic ye’elimite [2] and pseudo-cubic ye’elimite [3] were studied. Moreover, the hydration behaviour of both polymorphs with or without sulphate source was studied [21]. These studies unravelled that hydration kinetics of ye’elimite samples not only depends on the water/solid (w/s) ratio and the solubility of the additional sulphate source, but also on the polymorphism of ye’elimite. Firstly, in the absence of additional sulphate sources, orthohombic ye’elimite reacts slower than pseudo-cubic ye’elimite and the latter produces higher amounts of ettringite than orthohombic ye’elimite in similar hydrating conditions. Moreover, in this environment, the formation of AFm-type phases from orthohombic ye’elimite is strongly accelerated and favoured by high w/s ratios. Moreover, in presence of gypsum or anhydrite as additional sulphate sources, orthohombic ye’elimite reacts faster than pseudo-cubic ye’elimite. In addition, the formation of AFm-type phases at late ages is avoided by the addition of gypsum and anhydrite being ettringite the only crystalline phase formed in this reaction medium. Furthermore, the particle size [22], water content and the calcium uptake of amorphous aluminium hydroxide gels in ye’elimite eco-cements have been established with Ca contents being minor but not negligible [23].

4.2 Hydration of ye’elimite with ferrite.

The jointly hydration of ye’elimite and ferrite was also studied [24]. The hydration of a sample with ferrite, gypsum and orthohombic ye’elimite gives a mixture of AFT and AFm phases. However, CaAF hydration is slightly slowed down and moreover, these hydration products did not contain iron in their structures. The retarder effect of ye’elimite over C3A hydration was much stronger with pseudo-cubic ye’elimite and consequently AFT was the main hydration phase. CaAF was hydrated with ye’elimite in the absence of gypsum and gave Afm as the unique hydration product. Figure 4. Consequently, it was demonstrated that gypsum (which is a high soluble sulphate) was the main responsible for AFT formation in these systems.

4.3 Hydration of ye’elimite with belite and alite.

The reactivity of ye’elimite in the presence of both dicalcium silicate and alite has also been studied. Both polymorphs, α’H and β of dicalcium silicate were synthesized [25,26] and mixed jointly with both ye’elimites and gypsum. Moreover, mixtures of alite-ye’elimites and anhydrite were also prepared. The mixtures were hydrated. Table 2 gives the mineralogical composition, including amorphous contents (ACn) and free water (FW) of mixtures after 28 days of hydration of mixtures of C3S and ye’elimite with gypsum. In these experimental conditions the presence of belite in the mixture has not altered the hydration kinetics of ye’elimite. Pseudo-cubic ye’elimite (with a Dv50 of 5 µm) reacts at a higher pace than orthohombic (with a Dv50 of 9 µm) yielding higher amounts of AFT, Table 2. This last conclusion is also extensible to the mixtures containing alite.

Moreover, we have demonstrated that the hydration degree of α’H-C3S is much larger than that of β-C3S.

Table 2. Quantitative phase analysis results (wt%) of mixtures of orthohombic or pseudo-cubic ye’elimite (o-C3A1S or c-C3A1S), β-C3S or α’H-C3S with gypsum after 28 days of hydration obtained from LXRDP.

<table>
<thead>
<tr>
<th></th>
<th>β-C3S-</th>
<th>α’H-C3S-</th>
<th>β-C3S-</th>
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</tr>
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<tr>
<td></td>
<td>o-C3A1S</td>
<td>o-C3A1S</td>
<td>c-C3A2S</td>
<td>c-C3A1S</td>
</tr>
<tr>
<td>C3A1S</td>
<td>0.9(1)</td>
<td>2.6(1)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>α’H-C3S</td>
<td>-</td>
<td>13.9(4)</td>
<td>-</td>
<td>11.8(4)</td>
</tr>
<tr>
<td>β-C3S</td>
<td>20.6(2)</td>
<td>9.3(3)</td>
<td>20.1(2)</td>
<td>9.8(3)</td>
</tr>
<tr>
<td>Strat</td>
<td>6.5(3)</td>
<td>6.4(3)</td>
<td>6.7(2)</td>
<td>10.2(3)</td>
</tr>
<tr>
<td>AFT</td>
<td>21.1(2)</td>
<td>19.9(2)</td>
<td>23.5(2)</td>
<td>23.3(2)</td>
</tr>
<tr>
<td>ACn</td>
<td>0.5(1)</td>
<td>0.5(1)</td>
<td>0.5(1)</td>
<td>0.4(1)</td>
</tr>
<tr>
<td>FW</td>
<td>33.0(5)</td>
<td>31.8(6)</td>
<td>32.9(4)</td>
<td>32.7(6)</td>
</tr>
</tbody>
</table>

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