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Impact of quantity of anhydrite, water to binder ratio, fineness on kinetics and phase assemblage of belite-ye'elimite-ferrite cement

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ABSTRACT

One of the main challenge in belite, ye'elimite and ferrite cement is the control of the belite phase reactivity. We propose to study two mechanisms that impact belite hydration kinetic: the first mechanism is linked to available space for hydration products and can be seen as a decrease of water accessibility to cement surface and the second concerns the cement fineness. We used a thermodynamic model that can predict phase assemblage and we found good correlations between this model and the results obtained with XRD measurement and Rietveld refinement.

1. Introduction

BYF cements based on belite, ye'elimite and ferrite phases are alternative binders to Portland cement: these cements can lead to similar compressive strength development and produce lower amount of CO_2 released during their manufacturing. Indeed, conventional Portland cement manufacturing is highly energy and emissions intensive: about 850 kg of CO_2 is released in the atmosphere during the production of 1 ton of pure Portland clinker. Consequently, cement production accounts for 5% of all human-generated greenhouse emissions [1]. 60% of the CO_2 released by cement production is from the chemical breakdown of calcium carbonate (decarbonation). The remaining 40% of CO_2 is produced by the heating process, although the efficiency of this process has greatly improved over the years. Therefore, there are important challenges in finding ways to reduce the carbon footprint on concrete and cement manufacturing. One way to mitigate this carbon footprint is to replace part of the clinker or cement by alternative mineral powders called Supplementary Cementing Materials (SCMs). These materials are by-products or wastes, produced by other industries, like for instance coal fly ash or blast furnace slag but, artificial or natural pozzolans and limestone powders can be used to produce these blended cements as well. Blended cements could reduce CO_2 emissions by as much as 20%, but widespread use of blended cement is limited by environmental regulations, SCMs availability, costs and durability issues. The second alternative way is to produce an alternative clinker to Portland one that will require less limestone (calcium carbonate) amount in the raw mix. This is achieved with the so-called BYF clinker. In this clinker, belite phase (di-calcium silicate phase) is the main constituent following by ye'elimite (calcium sulpho-aluminate phase), and ferrite (calcium alumino-ferrite phase). These reactive phases are stable under similar production conditions and are characterized by their low CO_2 emissions during manufacturing [2–4]. Moreover, the firing temperature of BYF clinker is typically 1250 °C that is about 200 °C less than Portland one and, in addition, BYF clinker have better grindability [5,6]. So, all these characteristics lead to a global CO_2 reduction during clinker manufacturing of 20–25% compare to conventional pure Portland clinker. These BYF clinkers are different from conventional Chinese Calcium SulphoAluminate (CSA) clinkers which are used and standardized for more than 30 years [7,8]: BYF clinkers are mainly composed of belite phase in contrary of Chinese CSA which contains 60% and above of ye'elimite phase. Three industrials trials were successfully performed in Lafarge plants with conventional rotary kiln to produce BYF clinkers: two industrial trials using a hemi-dry process plant and one another trial using a dry process plant. Boron is also added into the raw mix to stabilize, during the burning process, a more reactive form of belite called α′-C_2S [9]. Contrary to Portland in which alite phase (C_3S) is the main phase responsible for the strength development, in the case of BYF cement, several important hydration reactions occur:

a) Ye'elimite reacts with calcium sulphate and free water to give rise to ettringite and aluminium hydroxide gel formation following Eq. (1) [10]:

$$C_4A_3\overline{S} + 2C\overline{S} + 38H \rightarrow C_3A.\ 3C\overline{S}.\ 32H + 2AH_3 \quad (1)$$

Depending on the water to cement ratio (W/C) and the amount of ye'elimite and calcium sulphate in the cement, this reaction will consume an important volume of initial water and the hydrates will fill quickly the initial porosity. The precipitated hydrates can be a mix

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of ettringite and calcium monosulpho-aluminate phases if the amount of calcium sulphate added does not fulfil Eq. (1). This reaction is generally completed after 1 or 2 days (and even earlier at 6 h) and thus will provide high early mechanical strengths: these strengths can be higher than those of Portland cement at same age.

b) Belite reacts with aluminium hydroxide previously formed in Eq. (1) and free water to give rise to strätlingite hydrate formation (see Eq. (2)) [11].

$$C_2S + AH_3 + 5H \rightarrow C_2ASH_8 \quad (2)$$

c) The increase of pH mainly due to belite hydration will destabilize strätlingite and this hydrate phase will react with the remaining belite phase to give rise to siliceous-hydrogarnet along with C-S-H hydrates following the global Eq. (3):

$$C_2ASH_8 + 2C_2S + 2.2H \rightarrow C_3AS_{1.3}H_{3.4} + 1.7C_{1.7}SH_4 \quad (3)$$

Some iron can be incorporated in siliceous hydrogarnet in substitution of alumina due the concomitant hydration of belite and ferrite phases [12].

d) After complete strätlingite destabilization and in the case of remaining belite phase and free water, C-S-H and portlandite (CH) hydrates can form following Eq. (4):

$$C_2S + 4.3H \rightarrow 0.3CH + C_{1.7}SH_4 \quad (4)$$

Strength development on EN standard mortar prepared from BYF cement (based on 52% belite, 28% ye'elimite, 20% ferrite) is similar to that obtained with OPC CEM I 52.5 [13]. However, contrary to Portland cement where alite phase hydration (C_3S) is mainly responsive for the strength acquisition, in the case of BYF cements, this strength acquisition follows mainly a two hydration steps process. Sometimes, in between these two main hydration steps process, we can note the formation of a strength plateau [14]: this strength plateau seems to start at the end of ye'elimite hydration phase usually after 1 or 2 days and ends up after about 7 days with the onset of belite hydration (Eq. (2)). So, this strength plateau arises when belite (and ferrite) hydration onset is delayed and that's why, there is an important challenge to get fast belite hydration kinetic in order to reduce as much as possible this “dormant” period. In this study, we focus on some levers that impact the time duration of this strength plateau. Thanks to XRD technique, we investigated the impact of the amount of calcium sulphate, of the water to cement ratio and of the cement fineness. For each lever and based on XRD results, the phase assemblages were determined as a function of time.

2. Experiment methods

2.1. Materials and mixed design

Table 1 shows mineralogy and density of five different BYF cements used in this study. The first three cements (BYF-A-2.5%, BYF-A-6.5% and BYF-A-15.5%) are based on a same clinker composition called BYF-Akk and all clinkers chemical compositions (main elements) are given in Table 2. Discrepancies may arise between the calculated mineralogy and the chemical composition that can be explained by:

- The accuracy of Rietveld quantification for anhydrous cement in our control file: +/− 2%,
- The suspected presence of non cristalline phases in the clinker not detected by XRD and, this will impact Rietveld quantification. In this calculation, we choose the hypothesis that the quantity of non-crystalline phases is negligible,
- The potential insertion of minor elements in anhydrous phases: we suspect iron insertion in ye'elimite phase that will not be taken into account in the Bogue calculation for instance.

For each clinker, boron was added in the raw mix (1.30% as B_2O_3 in clinker) in order to stabilize a more reactive form of belite called α′-C_2S. Ye'elimite, belite and ferrite are the main phases in clinker BYF-Akk but minor phases are also detected, mainly mayenite and gehlenite. Concerning cements BYF-A-2.5%, BYF-A-6.5% and BYF-A-15.5%, three different quantities of ground natural anhydrite were added to the same ground clinker to make BYF cements with a Blaine fineness of 4500 cm^2/g. Cements from BYF-A series were targeted for a study of the impact of quantity of anhydrite. In cement BYF-B, ye'elimite, belite and ferrite are the main phases but other phases as C_3FT (4,5%) and gehlenite (1,5%) are detected. BYF-B cement, with a Blaine fineness of 4200 cm^2/g, was used in a study of the impact of water to cement ratio (w/c) at 0.50 and 0.67. BYF-C cement was used to study the impact of fineness. The same BYF-Ckk clinker was ground to two different finenesses with all particles below 40 and 8 μm. Then, the same amount of ground natural gypsum (7%/cement) was added to these two ground clinkers. From thermodynamic point of view, we use a w/c 0.50 for all the sample, because based on the theoritical equations mentioned previously (Eqs. (1), (2) and (3)) and the cement composition given in Table 1, this water content is enough to form all hydration products. We are aware that our estimation is not complete because ferrite phase hydration is not taken into account in the calculation. However, we decided to neglect it due to the difficulty to assess its hydration pathway in a BYF cement. Nevertheless, in several cements like for instance BYF-A-2.5% and BYF-A-6.5%, the amount of free water needed is lower than this previous calculated value because there is not enough calcium sulphate to fulfil Eq. (1): in this particular case, a mix of ettringite and calcium monosulpho-aluminate phases is precipitated instead of pure ettringite and thus, lower amount of water is consumed.

Table 3 shows mix design of BYF cement pastes, ages of interest and types of tests. In every mix design, the kinetics of each mineral and phase assemblage are measured by a coupling method between XRD/Rietveld and Thermal Gravimetric Analysis (TGA). The XRD equipment was a PANalyticals X'Pert Pro diffractomer with a high speed “X'Celerator” detector. TGA measurements were done with around 100 mg of a “stopped” and dried ground cement paste, heated from 20 °C to 1000 °C at 20 °C/min in nitrogen atmosphere. The compressive strengths of cement pastes were measured only in the study of the impact of quantity of anhydrite.

2.2. Cement pastes

For cement paste, all materials and apparatuses were pre-conditioned at 20 °C. Water, and cement were mixed with a waring blender for 60 s at 3000 rpm. Paste stuck on the mixer bowl was put back in the

Table 1
Mineralologies (weight %) and density of BYF cements.

Cement reference	Ye'elimite	Belite	Ferrite	Anhydrite	Gypsum	Hemi-hydrate	Minor phases	Cement density (g/cm^3)
BYF-A-2.5%	28.1	49.4 (α′-C2S)	19.5	2.4	0	0	0.6	3.09
BYF-A-6.5%	27.3	47.5 (α′-C2S)	18.8	6.2	0	0	0.2	3.09
BYF-A-15.5%	25.2	42.4 (α′-C2S)	17.6	14	0	0	0.8	3.08
BYF-B	30.9	35.8 (α′-C2S = 32.8) (β-C2S = 3.0)	12.9	10	0.9	2.8	6.7	2.98
BYF-C	35.4	35.9 (α′-C2S)	20.9	0.7	7	0	0.1	3.02