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Effect of boron waste and boric acid addition on the production of low energy belite cement

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ABSTRACT

The effect of boron oxide addition on the production of low energy belite cements has been investigated. Three types of clinkers were prepared with 1.5 wt.% (BC_BA1.5) boric acid, and 1.0 wt.% (BC_BW1) and 6.5 wt.% (BC_BW6.5) boron waste addition. The design of the raw mixtures was based on modified Bogue equations. According to the free lime content and the evolution of the microstructure of the clinkers, firing was performed at 1330 °C, 1350 °C and 1310 °C for BC_BA1.5, BC_BW1 and BC_BW6.5, respectively. Boron addition favored the reduction of the clinkering temperature as well as the stabilization of upper belite polymorphs. According to the present results, late compressive strength development of belite cements depends mainly on the crystal type rather than on the content of belite in the clinker. The results indicate that controlled quantities of boron oxide can be beneficial in the production of belite cement.

1. Introduction

During 2007–2013, the global cement production followed an upward trend and its annual production will increase approximately 5–6% until 2018, boosted by construction sector. In 2013 worldwide production was 4 billion tons of cement, with China having the leading part [1,2]. As a result, cement industry is responsible for 5–7% of the worldwide CO_2 emission [3,4]. The environmental demand for reduction of CO_2 emissions, the increment of energy cost, the cost and requirement of raw materials, reinforce the need for the development of alternative, more environmentally friendly cements.

Belite-rich cement (BC) is an alternative type of cement, which has attracted scientific interest over the last 20 years [5,6]. BC, in contrary to conventional OPC, contains a higher percentage of belite and a lower percentage of alite which are the impure forms of dicalcium silicate (C_2S) and tricalcium silicate (C_3S), respectively. The different stoichiometry of alite and belite results in a decrease of the CO_2 emissions due to the lower $CaCO_3$ demand for the production of this type of cements. Moreover, C_3S is formed at temperatures greater than 1300 °C, while the formation temperature for C_2S is greater than 1000 °C [7]. The decrease of the BC production clinkering temperature results in energy savings up to 16% [8], which leads to further reduction of CO_2 emissions (up to 6–10%) [9,10].

Moreover belite cements develop high late compressive strength [11]. Therefore, the aforementioned environmental and mechanical benefits of the belite cements have arisen the industrial interest. High belite cements are already been produced and utilized in construction projects such as Three Gorges Dam, in China [12,13].

Despite the advantages, belite cements have a drawback which is the low early strength (up to 7 days) due to the low rate of hydration of C_2S [14,15]. It is proposed [14,16] that this drawback could be overcome with the stabilization of specific crystalline forms of belite, which poses improved belite's hydraulic properties. Belite crystallizes in five main structures [17,18] (α, α_H', α_L', β and γ) according to the temperature (Fig. 1). The crystalline forms of belite that possess better hydraulic properties i.e. are more “active”, are α, α_H', α_L' and β [16,18]. γ-C_2S form does not exhibit hydraulic properties. Moreover, it results in disintegration (dusting effect) due to the volume change, which occurs during the transition from β to γ belite [19]. Several belite “stabilizers” have been proposed in the literature [16,20,21]. Stabilization of the more “active” forms of belite can also be achieved by rapid cooling of the clinker [16].

Abbreviations: C, CaO; S, SiO_2; A, Al_2O_3; F, Fe_2O_3; B, B_2O_3; SM, silicate modules; AM, aluminum modules; LSF, lime saturation factor.

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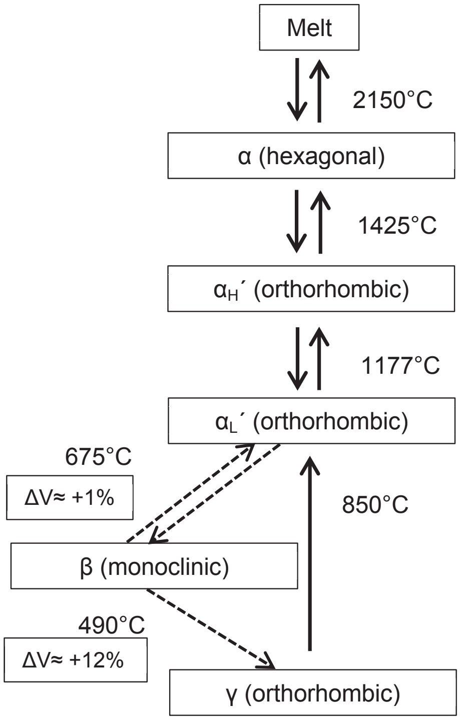

Fig. 1. Polymorphic transformations of belite with temperature and crystal systems [18].

Moreover, the stabilization could be accomplished by the incorporation of "stabilizer oxides" in the clinker, such as B_2O_3, Na_2O, K_2O, P_2O_3 etc. [20,21]. More specifically, the introduction of boron ions into the crystal lattice of C_2S, can stabilize α'- and β-polymorphs; α'-C_2S being more active than β-C_2S [16,20], thus preventing the formation of γ-form [22]. Although several research studies have been carried out about the stabilization of belite as a crystal, only a few have been referred to belite as part of the cement and to the use of B_2O_3 as stabilizer [23,24].

In the present work, the incorporation of boron oxide from two different sources, boric acid and boron waste, in the raw meal for the production of belite cement, as well as the effect of boron on the belite crystals as part of the clinker was studied. The clinkers produced were characterized by SEM/EDS and XRD. Water demand, initial setting time, and compressive strength were measured on both cement paste and cement according to EN-196.

2. Materials and methods

The raw materials used in the preparation of the raw meals were limestone and flysch. Two sources of boron were used: (i) boric acid, BA (H_3BO_3, Merck, purity 99.8%–100.5%) and (ii) boron waste, BW, from Kirka Boron Works in Turkey, containing 25.17wt.% B_2O_3. West Turkey possesses the largest boron deposits with a worldwide share of 72% (851 Mt) in terms of B_2O_3 content, and they are controlled by the national mining enterprise Eti Mine [25,26]. During this process, approximately 400,000 tons/year of different types of solid boron-containing wastes (BW) are formed and rejected in tailing dams next to the boron plant [27–30]. The B_2O_3 content in these wastes usually varies from 11 to 25 wt.%, which depends on the initial minerals and the processing conditions. The chemical analysis of the raw materials was performed by X-ray fluorescence spectrometry (XRF, Philips PW 2400) and is presented in Table 1.

The design of the raw meals was based on the predictions of the modified Bogue Eqs. (1)–(5). The Bogue equations were modified in order to comply with the system C–S–F-–A–B. Considering thermodynamic equilibrium, the oxides of the system were combined according to the following equations:

$$\%C_4AF = 3.043(\%Fe_2O_3) \quad (1)$$

$$\%C_5BS = 5.852(\%Fe_2O_3) \quad (2)$$

$$\%C_3A = 2.650(\%Al_2O_3) - 1.692(\%Fe_2O_3) \quad (3)$$

$$\%C_3S = 4.071(\%CaO) - 7.600(\%SiO_2) - 6.718(\%Al_2O_3) - 1.43(\%Fe_2O_3) \quad (4)$$

$$\%C_2S = 2.867(\%SiO_2) - 0.754(\%C_3S) \quad (5)$$

Based on the above Eqs. (1)–(5), the chemical analysis of the raw materials and the mass balances, a worksheet was developed in order to predict the synthesis of the raw meals according to the final clinkers, Table 2. Following the above methodology, three types of clinker were designed and tested: one with 1.5 wt.% (BC_BA1.5) boric acid addition and other two with 1wt.% (BC_BW1) and 6.5wt.%, (BC_BW6.5) boron waste, respectively.

The lime saturation factor (LSF) varied from 78% to 83% [16]. Alumina (AR) and silica ratios (SR) were maintained at 1.9% and 3.3%, respectively (Table 2), similar to those adopted in the production of OPC.

For the preparation of the clinkers, raw materials were individually milled in a Siebtechnik® planetary mill at a particle size below 90 μm. After thorough mixing and homogenizing, pellets of approximately 15–20 mm in diameter were formed by hand with a minimum addition of sprayed water. The pellets were dried for 24 h at 110 °C. Firing of the clinker was performed in a Nabertherm®, Super Kanthal resistance furnace at different temperatures.

Optimum clinkering temperature was determined by firing tests at 1280 °C, 1300 °C, 1320 °C, 1340 °C and 1360 °C with 40 min of soaking time. Free lime content was determined according to the ASTM C114-03 standard. Moreover as an indication of the quality of the clinker, the formation of different crystalline phases was evaluated by optical microscopy observation. For the stabilization of the hydraulic C_2S polymorphic forms, fast cooling was applied employing simultaneously blast air and crushing by means of a hammer.

The crystalline phases of the clinkers were identified by X-ray diffraction analysis (D5000 S). Diffraction patterns were measured in 2θ range of 5–70° using CuKa radiation of 40 kV and 30 mA, with a 0.01° step size and step time of 1 deg/min. SEM/EDS microanalysis (Jeol JSM 6300 and LINK PentaFET 6699, Oxford Instruments) of the clinkers was performed on gold-coated samples. Before coating, the samples were polished and subsequently etched 1% Nital.

For the preparation of the cement, clinker was milled by means of the aforementioned planetary mill to a finesse in the range of 4000–4100 cm^2/g. After milling, 5 wt.% gypsum with grain size lower than 90 μm was added. Specific surface (Blaine method) was measured according to EN 196-6 [31], setting time according to EN 196-3 [32] and compressive strength according to EN 196-1 [33].

3. Results

3.1. Characterisation of raw materials

The chemical analysis of the raw materials, namely limestone, flysch, BW and BA is presented in Table 1. Limestone and flysch have