



Active low-energy belite cement



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ABSTRACT

The term 'low-energy cement' is used for cements that can be in some applications used instead of OPC, and which are produced with less energy. A more extensive utilization of these cements would lead to the lowering of expenses on production of binders as well as a reduction of undesirable emissions. The belite-rich cement belongs to this group. Pure belite clinkers with interstitial matter consisting of C₃A and C₄AF have not been produced, as they have insufficient strength. This work describes the results of hydraulic activation of belite-rich clinkers with sulfate anions. The principle of activation is used for the preparation of belite-rich clinkers with an increased Ca:Si ratio in the structure of dicalcium silicate and partial substitution of SiO₄⁴⁻ by SO₄²⁻. Cements, prepared from these belite-rich clinkers, containing up to 20% of alite, which are burned at 1350 °C, have the same technological properties, including early strengths, as OPC.

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1. Introduction

The research and the production of hydraulically active low-energy cements, especially those based on belite-rich clinkers, are very topical and for the future of cementitious binders highly prospective. It is expected to be one of the main directions in the development of the world cement industry.

Mass production of low-energy cements would mean a considerable decrease in the total expense of cement production when compared to the current common Portland cement with high alite content. It would also mean an overall decrease in the environmental impact of cement production. This attenuated impact can be seen rather in the decrease of CO₂ emissions owing to the composition of the raw meal for the production of low-energy clinkers, as they require less CaO and thus less consumption of CaCO₃, than in reduction temperature of burning by 100–300 °C. This approach supports sustainable development of high-quality raw materials – notably pure limestones – by facilitating the use of resources of a lesser grade with lower CaCO₃/higher impurity content. It also encourages the (re-)utilization of industrial by-products and/or wastes.

Belite in the common Portland clinker has considerably lower hydraulic activity than alite [1] and contributes significantly to strengths only after 28 days of hydration. This led to efforts to stabilize hydraulically active forms of belite, specifically related to high-temperature modifications. A chemical stabilization by suitable admixtures, usually complemented by fast quenching [2–5] is one of the possibilities. A newer method of belite hydraulic activation is a utilization of the

'remelting reaction' [6,7] or 'sol-gel method' [8,9]. Such methods can be realized only under conditions outside the possibilities of currently used industrial technologies. The research of the mechanism and kinetics of belite clinker formation has shown, that a quickly formed belite clinker has, in contrary to original expectations, lower hydraulic activity than a longer burned, recrystallized belite clinker [10].

Production of sulfoaluminate-belite (SAB) cement is performed to a limited extent, as these cements show appropriate properties [11,12]. Experiments with industrial production of the sulfo-aluminate-ferrite belite clinker (SAFB) and the high-Fe belite clinker (HFBC) gave cements with satisfactory strengths after 28 days of hydration, but low short-term strengths [13].

China has made great progress in testing such technologies with industrial production of SAB and also fluoroaluminate belite cement and high belite Portland cement with 20–30 wt.% alite [14].

The main problem to be solved is the production of hydraulically active belite cement, with properties like those of standard "alite" Portland cement, using the existing production lines.

The principle of activation is the formation of a belite clinker with an increased ratio of CaO:SiO₂ in the structure of dicalcium silicate by substitution of SiO₄ groups by SO₄ groups. SO₃ considerably decreases the viscosity and surface tension of the clinker melt [15,16]. It postpones the start of alite formation and decreases its nucleation and its overall content in the clinker. It can completely block alite formation [17–19]. Beyond this, it supports the formation of belite and enters in quantities into the belite structure. This fact can be used in the preparation of relatively high saturated belite clinkers. A relatively high saturation of a belite clinker (high content of CaO in the belite structure) ensures in the ensuing reaction with water the formation of increased portlandite (Ca(OH)₂) and an overall alkalinity, accelerating the course of its hydration.

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In practice, waste desulfurization products and fluidized bed fly ash can be used in the burning of the 'sulfobelite' clinker. This clinker, burnt at lower temperatures, would not contain a greater extent of C_4A_3S calciumsulfoaluminate (Klein's complex, yeelimite) – in comparison with SAB cement.

2. Material and methods

The raw materials used in the preparation of experimental raw meals were pure limestone with 97.5 wt.% $CaCO_3$ (L1), limestone with increased SiO_2 content – 30 wt.% (L2), clay shale with 41.5 wt.% SiO_2 and 12.5 wt.% Al_2O_3 (CS), pure quartz with 99.5 wt.% SiO_2 (Q), roasted pyrite as iron correction (Fe), and flue-gas desulfurization (FGD) gypsum. The composition and expected chemical parameters of the raw meals are given in Tables 1–3. The planned experiments involved the burning of belite clinkers with 4, 5, 6 and 8 wt.% of SO_3 in the raw meal and a different lime saturation index, the referenced low-saturation belite clinker, and referenced alite clinker without SO_3 addition.

Six kilograms of each raw meal mixture were ground until ~12 wt.% fraction passed <0.09 mm. The raw meals were pressed into tablets 4 cm in diameter, weighing about 80 g. All belite clinkers were burned in a super-kanthal furnace in the following regime: rate of temperature rise 15 °C/min, final temperature 1350 °C or 1400 °C, and isothermal dwell time 30–60 min. The alite clinker was burned at 1450 °C for 120 min.

Representative amounts of the clinkers thus produced were comminuted to <1 mm and sieved. Polished epoxy mounts of fractions 0.045–1 mm were etched in fumes of acetic acid for reliable phase identification [20]. Modal content of constituent phases was determined using optical microscopy and point counting of 2000 points per section [21]. For the recalculation from volume to weight percentages, the following densities were used: C_3S – 3.15, C_2S – 3.28, C_3A – 3.03, C_4AF – 3.77, and free CaO – 3.35 $g\cdot cm^{-3}$.

After re-polishing, the sections were analyzed with an electron microprobe (CAMECA SX100 with 5 crystal spectrometers) to determine the chemical composition of the clinker minerals. The quantitative spot analyses were performed under the following analytical conditions: accelerating voltage 15 kV, probe current 20 nA, and spot size 2 μm . The standards used for internal calibration were natural standards – wollastonite (Ca, Si), barite (S), orthoclase (K, Al), andradite (Fe), jadeite (Na), rhodonite (Mn), pyrope (Mg), hydroxylapatite (P), and synthetic TiO (Ti); all elements were analyzed on their $K\alpha$ lines. The lower limits of detection varied between ~0.01 wt.% (e.g. for P, S, Si, Al, Ca) and ~0.02 wt.% (e.g. Ca, K, Mn, Fe). The acquired counts, corrected for background, were recalculated to oxides using the PAP correction procedure included in the CAMECA PeakSight automation program. The EMPA results in wt.% oxides were recast into composition formulae in atoms per formula unit (apfu) according to the method described in [22].

Table 1

The composition of reference raw meals without the addition of SO_3 in wt.% and expected basic chemical parameters.

Raw meal	B75S0	B81S0	A95S0	A97S0
L1	55.27	69.70	64.41	71.83
L2	19.59	–	14.10	–
CS	23.72	22.56	20.62	23.40
Q	–	6.74	–	3.73
Fe	1.42	1.00	0.87	1.04
EG	–	–	–	–
LSF	75	81	95	97
SR	2.6	3.2	2.6	2.6
AR	1.4	1.5	1.6	1.5

Table 2

The composition of raw meals with the addition of 4 and 5 wt.% SO_3 in wt.% and expected basic chemical parameters.

Raw meal	B86S4	B80S5	B85S5	B89S5	B89.5S5	B90S5
L1	66.20	48.82	52.74	65.22	65.35	65.48
L2	–	18.92	17.51	–	–	–
CS	21.02	22.96	20.57	21.29	21.19	21.09
Q	6.30	–	–	5.61	5.59	5.56
Fe	0.89	1.37	1.26	0.89	0.88	0.88
EG	5.59	7.92	7.92	6.99	6.99	6.99
LSF	86	80	85	89	89	90
SR	3.2	2.6	2.6	3.2	3.2	3.2
AR	1.5	1.4	1.4	1.5	1.5	1.5

Qualitative determination of sulfate phases was done by powder X-ray diffraction of the clinkers with a Bruker D8 Advance diffractometer with variable slits and a position sensitive detector. The diffractometer was operated at 40 kV and 30 mA, using Ni-filtered $CuK\alpha$ of $\lambda = 1.541,718 \text{ \AA}$, recording 6–80° in $0.02^\circ 2\theta$ increments with 188 s counting time per step and total scan time of 1 h 5 m 59 s. β - C_2S unit cell parameters were refined by the Rietveld method using the Topas 3 software.

Finally, 2–4 wt.% of natural gypsum was added as a setting controller to all belite clinkers ground to produce cement with similar specific surface areas. These cements were then subjected to testing of their compressive and flexural strength and heat of hydration according to EN 196 standards.

3. Results and discussion

3.1. Composition of clinkers

The result of the quantitative phase composition of all clinkers, the major oxides contents and the real basic chemical parameters (LSF, SR, AR) is given in Tables 4–6. These tables also contain further data about the clinker burning (temperature and burning time) and on the properties of cements prepared from them. The microstructure of the belite-rich clinker doped with SO_3 is exemplified by Fig. 1.

The chemistry of belite grains was determined by electron microanalysis. The results are given in Tables 7–9. The charge sums for the cations and the framework elements are also included there. Compared with the composition of belite in common alite-rich clinkers, reported by various authors [23–25], belites from our experiments exhibited an elevated Ca/Si ratio (ranging from 2.4 to 2.6), that correspond to the partial substitution of Si by S. In common belites it is much closer to 2 (1.9 to 2.18). Herfort et al., who also experimented with burning raw meals enriched with sulfur [26], reported belites with atomic Ca/Si ratio between 2.37 and 2.42.

Table 3

The composition of raw meals with the addition of 6 and 8 wt.% SO_3 in wt.% and expected basic chemical parameters.

Raw meal	B89S6	B90S6	B91S6	B92S6	B96S6	B98S6	B92S8
L1	64.49	64.75	64.97	65.24	66.21	66.67	62.72
L2	–	–	–	–	–	–	–
CS	20.19	19.99	19.79	19.60	18.85	18.49	19.42
Q	6.07	6.02	6.00	5.93	5.75	5.66	5.85
Fe	0.86	0.85	0.85	0.84	0.80	0.79	0.83
EG	8.39	8.39	8.39	8.39	8.39	8.39	11.18
LSF	89	90	91	92	96	98	92
SR	3.2	3.2	3.2	3.2	3.2	3.2	3.2
AR	1.5	1.5	1.5	1.5	1.5	1.5	1.5

Where: LSF – lime saturation factor after Lea–Parker, SR – silica ratio, AR – alumina-iron ratio.

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