

Quantitative Phase Analysis of Belite Portland Cements from Synchrotron X-ray Powder Diffraction

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1. Introduction.

Cement manufacture processes need vast amounts of energy, especially to burn cement clinker and to grind raw and produced materials. This power consumption leads to a concomitant release of CO₂ into atmosphere, up to 0.97 tons of CO₂ per Ordinary Portland Cement (OPC) produced. Considering these values, cement industry contributes around 6% of all CO₂ anthropogenic emissions [1,2].

The increasing interest of Belite Portland cements (BPCs) and related systems is mainly due to a lower CaCO₃ consumption and therefore the depletion of CO₂ emissions produced in the manufacturing process [3-5]. Ca₂SiO₄ is the main mineralogical component of BPCs (more than 50 wt%) while the most important phase in OPCs is Ca₃SiO₅, alite. BPCs can be produced at a clinkerization temperature approximately 100°C lower than that for OPC, which reduces CO₂ emissions from fuel burning [6]. The application at industrial scale of these materials requires overcoming some drawbacks such as the low hydration rate of the belite phase and high resistance to be milled [2,7]. BPCs based concretes are considered to be “low heat” ones and more durable than those derived from OPC. These performances make BPCs suitable to the construction of large dams and to the lining of oil wells.

Stoichiometric C₂S presents five polymorphs on heating, see Figure 1.

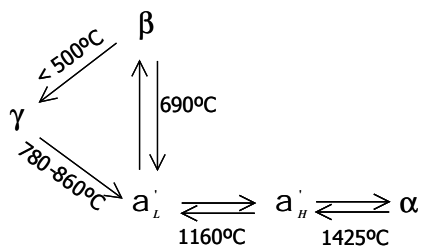


Figure 1. Polymorphic transformations of pure Ca₂SiO₄ with temperature [8].

One kind of activation of BPCs consists on the stabilisation at room temperature of the high temperature polymorphs (i.e. α forms), which are

more reactive than β -C₂S [9]. The latter is the polymorph that commonly prevails in OPCs but due to its slow hydration kinetic and it develops very little mechanical strength at early ages. The activation may be carried out by conventional firing using minor elements (dopants/activators) such as alkalies, sulphur or barium additions [3] or by special thermal treatments [10,11]. The stabilisation of α -forms using alkalies was reported in previous studies [12]. The presence of an increasing amount of alkaline oxides in the BPCs (active-BPCs) yielded higher compressive strengths after 28 days when compared with alkali-free BPCs. Furthermore, sulphur is also commonly present in clinkers, mainly coming from fuels. This element is mainly dissolved in the melt that appears in the clinkerization procedure and it has a positive effect on the burnability of the raw mix [13]. On the other hand, sulphur also leads to a lattice modification of β -C₂S with improved hydraulic properties and it has been reported that the stabilisation of α -forms cannot be achieved by this element [14].

Final concrete performances depend on the mineralogical phase composition (and the texture properties). Quantitative phase analysis (QPA) of active-BPCs is very important and X-ray powder diffraction (XRPD) combined with the Rietveld method [15] is the most powerful tool to carry out this type of analysis. High-resolution synchrotron XRPD overcomes or minimise most of the inherent drawbacks of laboratory XRPD such as poor sample averaging, microabsorption or preferred orientation [16,17].

Belite-rich clinkers with C₂S contents close to 60 wt% were prepared and analysed by QPA and laboratory XRPD [18] as an initial step in our research in this topic. In that study, β -C₂S was the main polymorph due to absence of dopants. This work presents a summary of the investigations of activation of belite-rich Portland clinkers [19], including, white belite Portland ones. Here we give Rietveld QPA of clinkers activated with alkaline oxides, sulphur and a combination of them. Belite Portland cements have been analysed using synchrotron XRPD data and white Belite Portland clinkers are analysed with Laboratory XRPD. The influence of alkaline oxides and sulphur in the mineralogical phase assemblage is discussed.

2. Experimental section.

2.1. Samples preparation.

Two series of belite-rich clinkers were prepared: Belite Portland clinkers (hereafter labelled as B_{*}) and White Belite Portland clinkers (hereafter labelled as WB_{*}). Initial raw mixtures to obtain B_{*} were prepared by mixing appropriated amounts of calcite (99% Aldrich), kaolin (Aldrich), quartz (99.59% ABCR) and iron oxide (99.95% Alfa Aesar). On the other hand, to obtain WB_{*} iron oxide was not added. To promote activation, in

both series, K_2CO_3 (99% Aldrich), Na_2CO_3 (99.999% Aldrich) and/or pure gypsum were added. The dosages, as oxides, used to prepare each clinker are shown in Table 1. The theoretical mineralogical composition of Belite Portland clinkers was 60% of C_2S , 16% of C_3S , 8% of C_3A , 16% of C_4AF , and that of White Belite Portland clinkers was 60% of C_2S , 26% of C_3S , 14% of C_3A .

Raw materials were mixed by hand in an agate mortar with ethyl alcohol and dried in a stove at 60 C. This treatment was performed by triplicate.

The clinkerization for all Belite Portland clinkers was carried out by pressing the raw mixtures into pellets of ~1.8 g with ~16 mm of diameter. The pellets were placed on Pt/Au crucibles and heated at 5°C/min to 900°C, which was held for 30 min. The temperature was then raised at a rate of 5°C/min up to 1365°C and held for 15 min. Finally, the clinkers were cooled from the highest temperature applying air flow (approximate rate cooling of 2000°C/min).

White Belite Portland clinkers were prepared as previously described except for the clinkerization temperature, which was higher, 1450°C.

Table 1. Dosages used to obtain the different belite clinkers, expressed as oxide in weigh percent. The amount of activator added is highlighted in bold.

Sample	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	K ₂ O	Na ₂ O	MgO	SO ₃
B_ref	62.81	25.00	6.34	5.23	0.27	0.13	0.07	0.01
B_1.0K	62.35	24.81	6.29	5.19	1.01	0.13	0.07	0.01
B_2.0K	61.74	24.56	6.23	5.13	2.01	0.12	0.06	0.01
B_0.5N	62.59	24.90	6.31	5.21	0.27	0.50	0.07	0.01
B_1.5N	61.97	24.65	6.25	5.15	0.26	1.50	0.07	0.01
B_0.8S	62.72	24.74	6.27	5.17	0.08	0.12	0.00	0.81
B_1.0S1.0K	62.01	24.39	6.18	5.10	1.00	0.12	0.06	1.01
B_1.0S2.0K	61.38	24.14	6.12	5.05	2.00	0.12	0.06	1.01
B_1.0S0.5N	62.21	24.48	6.21	5.12	0.26	0.50	0.07	1.01
B_1.0S1.5N	61.61	24.23	6.14	5.07	0.26	1.50	0.06	1.01
WB_ref	66.53	27.61	5.25	0.07	0.22	0.13	0.06	0.01
WB_1.0K	66.01	27.39	5.21	0.07	1.01	0.13	0.06	0.01
WB_2.0K	65.34	27.11	5.16	0.07	2.01	0.13	0.06	0.01
WB_1.0N	65.95	27.37	5.21	0.07	0.22	1.00	0.06	0.01
WB_2.0N	65.29	27.09	5.15	0.07	0.22	2.00	0.06	0.01

2.2. Selective dissolution of belite clinkers.

Some clinkers were chemically treated using the selective dissolution methods in order to make partial separation of the clinker phases. A solution of sucrose in aqueous potassium hydroxide was used to prepare the silicate enriched residue, which mainly contains C_2S and C_3S [20,21]. The salicylic acid in methanol method was performed to obtain the aluminate enriched residue, which mainly contains C_3A and C_4AF [20,21].

2.3. Chemical analysis.

The activators are volatile and its volatilisation rate depends upon experimental conditions. Thus, the final Na and K contents in clinkers were determined by atomic emission spectroscopy in a Perkin-Elmer AAnalyst 800. The final sulfate content was measured by gravimetric method in accordance with EN 196-2.

2.4. X-ray powder diffraction data collection.

Synchrotron XRPD patterns have been collected on ID31 diffractometer in Debye-Scherrer (transmission) configuration of ESRF, European Synchrotron Radiation Facility, (Grenoble, France). The wavelengths were selected with a double-crystal Si (111) monochromator and calibrated with Si NIST ($a=5.431195 \text{ \AA}$). To record the patterns for B_ref, B_1.0K, B_2.0K, B_0.5N, B_1.5N and the enriched residues, $\lambda=0.620706(2) \text{ \AA}$ (19.98 keV) was used. On the other hand, $\lambda=0.40084(5) \text{ \AA}$ (30.94 keV) was selected to collect the patterns for B_0.8S, B_1.0S1.0K, B_1.0S2.0K, B_1.0S0.5N and B_1.0S1.5N. All these samples were loaded in borosilicate glass capillaries of diameter of 1.5 mm and rotated during data collection. The data acquisition time was ≈ 45 min to have very good statistics over the angular range $1.0\text{-}30^\circ$ (in 2θ). The data from the multi-analyser Si(111) stage coupled with seven scintillation detectors were normalised and summed up to 0.003° step size with local software to produce the final raw data.

Laboratory XRPD patterns were recorded for WB_ref, WB_1.0K, WB_2.0K, WB_1.0N and WB_2.0N in a Bragg-Brentano (reflection) X'Pert MPD PRO diffractometer (PANalytical) using $\text{CuK}\alpha_1$ radiation ($\lambda=1.54059\text{\AA}$), [Ge(111) primary monochromator]. The optics used were a fixed divergence slit ($1/2^\circ$), a fixed incident antiscatter slit (1°), a fixed diffracted anti-scatter slit ($1/2^\circ$) and an X'Celerator RTMS (Real Time Multiple Strip) detector, working in scanning mode with maximum active length. The data were collected from 10° to 70° (2θ) during ~ 2 hours. The samples were rotated during data collection at 16 rpm in order to enhance particle statistics. The X-ray tube worked at 45 kV and 35 mA.

All the patterns were analysed by using the Rietveld method as implemented in the GSAS software package [22]. Peak shapes were determined by using the *pseudo*-Voigt function [23] with the axial divergence correction implemented [24].

3. Results and discussion.

3.1. Polymorphism determination.

All phases present in clinkers crystallize in different polymorphs. To perform accurate QPA using Rietveld methodology is essential to choose the best structural description for each phase. Selective dissolutions were carried out for B_ref, B_1.0K, B_2.0K and B_1.5N in order to determine the polymorph present of each phase as a function of elemental composition. In order to minimize errors in QPA results, synchrotron XRPD data was collected for these clinkers and their enriched residues.

Analysing the silicate enriched residues, obtained by treating clinkers with sucrose and potassium hydroxide solution, the absence of γ -C₂S form has been confirmed. This is the hydraulically inactive room temperature form of C₂S and its presence is undesirable in clinkers. The polymorphic transformation $\beta \rightarrow \gamma$ of C₂S on cooling has been avoided by shortening residence time at high temperature [18].

Rietveld analysis of silicate enriched residue of the clinkers treated confirmed the presence of β -C₂S [25], α'_H -C₂S [26] and α -C₂S [25]. The latter is the highest temperature polymorph and was not present in B_ref. Figure 2(a) displays a selected range of the Rietveld plots of B_2.0K clinker and Figure 2(b) shows the same selected range of the Rietveld plot of the silicate enriched residue of the same clinker. Main peaks due to a given phase have been labelled.

Belite clinkers synthesized in this work are expected to contain more than 15 wt% of C₃S. So, it is very important to model this phase properly. Stoichiometric C₃S presents seven polymorphs with increasing temperature [27,28]. We have found that the room temperature polymorph of C₃S, which is triclinic [29], was present in all residues except for B_1.5N. In this last sample, the alite pattern was different and the structural description of M₃-form [30] was used. We must highlight that MgO-source was not added to the raw mixtures in this study.

Salicylic-methanol method was used to dissolve C₂S and C₃S leaving the aluminates fraction. Figure 2(c) displays a selected range of the Rietveld plot of the aluminate enriched residues of B_2.0K. The iron rich phase Ca₂(Fe_{2-x}Al_x)O₅ was fitted with the structural description with $x=1$, C₄AF [31] in most of the clinkers. Some of the clinkers also needs to use another member of the solid solution with $x=1.346$ [32], and it will be labelled hereafter C₄AF-I.

Stoichiometric C₃A is cubic and does not present polymorphism. Nevertheless, the presence of foreign ions induces some structural modifications. The best structural description for the synchrotron XRPD pattern of C₃A in the B_ref aluminate residue was the cubic CII pseudo-polymorph [33]. The synchrotron XRPD patterns of the B_1.0K and B_2.0K aluminate residues clearly showed a mixture of cubic CII-C₃A and orthorhombic-C₃A [33]. Finally, only orthorhombic-C₃A was observed in the B_1.5N residue.

These results will be taken into account to perform the QPA of the remaining clinkers.

3.2. Chemical analysis.

Some methodologies for the activation of BPCs require the dosage to the raw mixtures of volatile compounds. Thus, the liberation of a fraction of the activators added is a potential fact on the heating process. To approach that issue, Na, K and S contents have been measured in the final c linkers; see Table 2, where they are expressed as oxides. It can be seen that sodium mainly remains in the all the clinkers, B_* and WB_*, with little volatilisation ratio in the used experimental conditions.

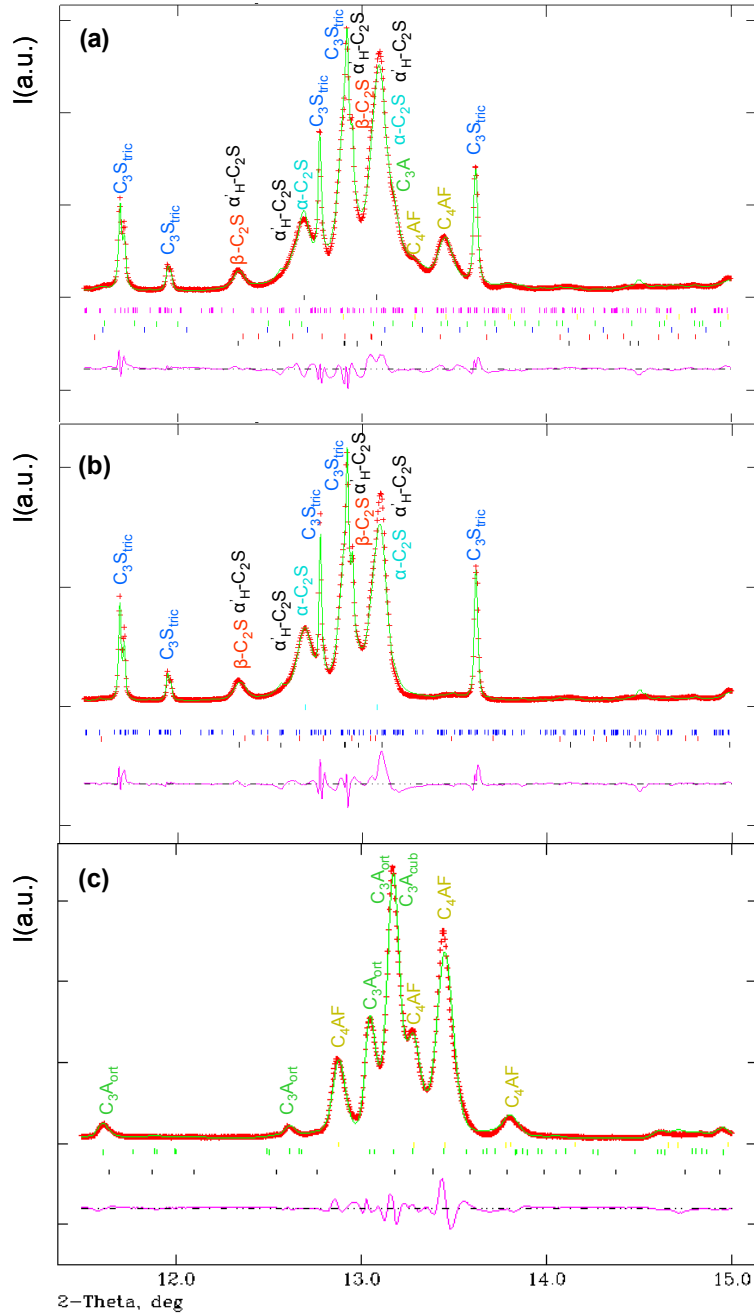


Figure 2. Selected range of the Rietveld plots for (a) B_2.0K belite clinker, (b) B_2.0K silicate enriched residue and (c) B_2.0K aluminate enriched residue. Peaks mainly due to a given phase have been labelled.

However, the losses of potassium and sulphur are higher. Potassium volatilisation extent can be as high as 50% and it is rather variable. On the other hand, sulphur volatilisation amount is comparatively much smaller ranging between 10-20%. However, it must be highlighted that element volatilization levels strongly depend upon the heating experimental conditions including the ratio between gases and raw materials. Hence, further studies are needed to extrapolate these results to industrial applications.

Table 2. Final S, K and Na contents in laboratory active belite clinkers. Results are expressed as oxides in weigh percent.

Sample	K ₂ O/%	Na ₂ O/%	SO ₃ /%
B_ref	0.04	0.16	--
B_1.0K	0.38	0.09	--
B_2.0K	1.48	0.12	--
B_0.5N	0.07	0.51	--
B_1.5N	0.11	1.16	--
B_0.8S	0.06	0.20	0.71
B_1.0S1.0K	0.67	0.23	0.87
B_1.0S2.0K	1.10	0.25	0.79
B_1.0S0.5N	0.19	0.64	0.85
B_1.0S1.5N	0.19	1.28	0.79
WB_ref	0.01	0.20	--
WB_1.0K	0.13	0.17	--
WB_2.0K	0.32	0.19	--
WB_1.0N	0.00	0.74	--
WB_2.0N	0.02	1.30	--

3.3. Quantitative phase analyses of active belite clinkers.

Rietveld QPA results of all the Belite Portland clinkers prepared in this study are given, in Table 3.

The first result to be emphasized is the absence in most of the clinkers of free lime (CaO) which indicates that thermal treatment was appropriate. In all laboratory belite clinkers (B_* and WB_*) β -C₂S was present. The stabilisation of this phase is due to the rapid cooling rate, the low particle sizes and the presence of foreign ions into its structure. It has to be noticed that increasing contents of activators help α' _H-C₂S stabilisation, with the concomitant decrease of β -C₂S percentage. Potassium oxide, in the absence of sulphur, has promoted α -C₂S stabilisation in B_1.0K and B_2.0K, see Table 3. On the other hand, in WB_1.0K this phase is not

present and WB_2.0K has only 3.9(3) wt%. This fact is mainly due to the higher volatilization rate of potassium in white belite clinkers than in iron-containing ones, see Table 2. Na₂O-bearing belite clinkers contain high amounts of α forms. Sodium oxide also favours the crystallisation of larger amounts of C₃S, and this effect is enhanced in the presence of sulphur, see B_1.5N and B_1.0S1.5N in Table 3. However, Na₂O also promotes the formation of large amounts of C₃A, see Table 3. It was reported [14] that the stabilisation of α -forms of C₂S could not be achieved by SO₃ contents up to 1.5 wt%. In this work, the stabilisation of 6.7(2) wt% of α' -C₂S has been accomplished only with 0.71 wt% of SO₃ in B_0.8S, see Table 2 and Table 3. It is known that the role of K₂O and Na₂O in phase stabilisation is not the same. In Figure 3, raw patterns of all belite clinkers are presented. Main peaks due to a given phase have been labelled. The use of high resolved data (synchrotron and strictly monochromatic laboratory radiations) and the previous study with selective dissolution method have aided to determine the presence of both triclinic and monoclinic C₃S in some clinkers as well as the coexistence of cubic and orthorhombic C₃A, see Table 3. The formation of alkaline sulphates strongly depends on the manufacturing process. In this study, belite clinkers have been prepared in a static electric furnace, thus the amount of minor phases, i.e. K₂SO₄ and/or K₃Na(SO₄)₂ are small, see Table 3. At an industrial stage, the stabilisation of sulphate phases may be more important due to the different gases-to-raw materials ratio.

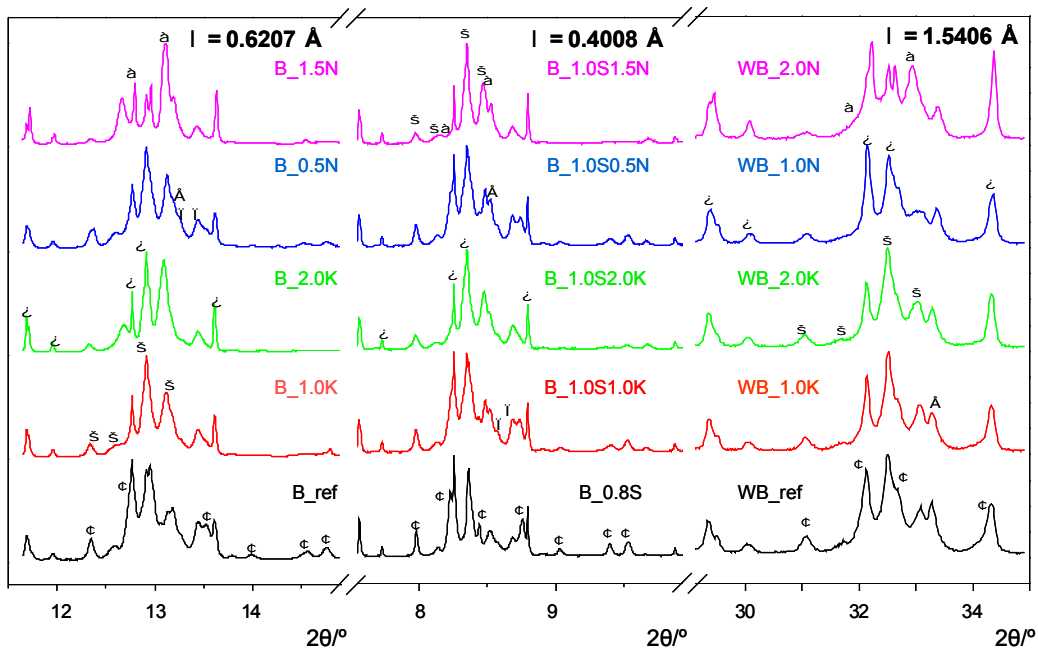


Figure 3. Selected range of raw data of all studied clinkers. Some peaks mainly due to a given phase are labeled: β -C₂S ■, α' -C₂S s; α -C₂S à; C₃S c, C₄AF i and C₃A ~.

Table 3. Rietveld quantitative phase analysis results of B_* in wt% obtained from synchrotron XRPD data and WB_* from laboratory XRPD.

Sample	a-C ₂ S	a' _H -C ₂ S	b-C ₂ S	C ₃ S _T	C ₃ S _{M3}	C ₃ A _{CII} / C ₃ A _{ort}	C ₄ AF/ C ₄ AF-I
B_ref	–	18.5(2)	46.7(1)	9.3(2)	3.9(2)	10.1(1)/ –	11.5(1)/ –
B_1.0K ^{&}	5.0(1)	39.4(2)	17.9(2)	15.4(1)	–	2.15(3)/ 8.3(1)	11.5(1)/ –
B_2.0K	19.2(1)	35.9(1)	4.5(2)	17.6(1)	–	2.9(1)/ 10.3(1)	9.6(1)/ –
B_0.5N	4.3(1)	32.9(1)	26.0(1)	7.5(3)	7.4(3)	9.0(1)/ 2.5(1)	10.4(1)/ –
B_1.5N	28.7(2)	10.3(3)	14.8(1)	–	20.6(1)	–/ 17.4(2)	8.2(1)/ –
B_0.8S	–	6.7(2)	60.74(8)	12.26(7)	–	9.1(1)/ –	8.4(1)/ 2.8(1)
B_1.0S1.0K [§]	–	23.9(1)	41.7(1)	12.72(7)	–	9.0(1)/ –	9.4(1)/ 2.47(8)
B_1.0S2.0K [#]	–	37.7(2)	23.5(2)	15.37(8)	–	8.8(1)/ 2.1(1)	8.9(1)/ 2.7(1)
B_1.0S0.5N	–	28.0(1)	39.9(1)	11.36(7)	–	9.72(9)/ –	8.92(9)/ 2.10(8)
B_1.0S1.5N	5.0(1)	42.0(2)	12.2(3)	17.00(8)	–	–/ 13.5(1)	8.1(2)/ 2.2(1)
WB_ref	–	28.0(3)	36.7(3)	24.3(2)	–	11.0(2)/ –	–
WB_1.0K	–	35.6(2)	26.3(3)	17.1(5)	10.8(5)	10.2(2)/ –	–
WB_2.0K ^{**}	3.9(3)	41.0(3)	17.2(4)	14.5(6)	13.9(6)	8.9(2)/ –	–
WB_1.0N	–	31.6(3)	25.3(4)	21.8(6)	10.6(7)	4.5(2)/ 6.2(2)	–
WB_2.0N [@]	16.4(4)	16.7(8)	23.2(6)	6.0(6)	26.7(5)	–/ 9.5(2)	–

[&] Also contains 0.35(2) wt% of CaO. [§] Also contains 0.29(3) wt% of K₂SO₄ and 0.52(4) wt% of K₃Na(SO₄)₂. [#] Also contains 0.93(4) wt% of K₂SO₄. ^{**} Also contains 0.60(5) wt% of CaO. [@] Also contains 1.50(5) wt% of CaO.

4. Conclusions.

The activation of belite clinkers by stabilizing high temperature (α'_H and α) polymorphs of C₂S has been achieved by adding alkaline cations and/or sulfur. The presence of alkaline oxides, Na and K, led to large amounts of α -C₂S, in some cases larger than 25 wt%. The joint existence of alkaline oxides and SO₃ promotes large quantities of α'_H -C₂S, but the presence of SO₃ inhibits the crystallisation of α -C₂S.

5. References.

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