New Alkaline-Belitic hybrid binders

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ABSTRACT

This paper summarises a long-term study organized in two consecutive steps. The first, which involved exploring a number of laboratory-synthesised belite clinkers with slightly different mineral compositions in depth, culminated in the industrial-scale manufacture of one of those materials. In the second a hybrid alkaline belite cement was prepared containing 48 % of the industrial belite clinker, 48 % fly ash and 4 % chemicals. The hybrid binder was subsequently analysed to determine its mechanical strength and hydration products. The findings showed that the hybrid alkaline belite cement designed met the compositional, mechanical and setting time requirements laid down in European standard EN 197-1 and that its hydration favoured the simultaneous precipitation of a mix of cementitious gels: C-(A)-S-H and N-(C)-A-S-H.

1.   INTRODUCTION

Interest in belite cements arose in the wake of the nineteen seventies energy crisis (Sark et al. 1981, Nagaoka et al. 1994, Chatterjee 1996), for these cements have a lower lime saturation factor than ordinary portland cement (LSF≤90) and C_2S can be manufactured at approximately 200 °C below the temperature needed to form C_3S. As a result of those two particulars, belite cement production requires less energy and entails lower CO_2 emissions than ordinary portland cement manufacture (Chatterjee 1996, García-Díaz et al. 2011).

As a rule belite cement yields more durable concretes than ordinary portland cement (OPC), for its hydration is associated with the generation of more basic conditions. These cements are more difficult to grind, however, and their hydration kinetics are slower than in OPC (Propescu ef al 2003, Staněk and Sulovský 2015).

The scientific community has adopted a number of approaches to activate belite cements with a view to enhancing their reactivity and consequently their early age strength development. Thermal activation of C_2S (for instance) is related to clinker cooling, which plays a key role in polymorphic transformation (reactivity varies from on polymorph to another) and in increasing C_2S specific surface (Staněk and Sulovský 2015).

In the chemical activation of belite, the crystalline structure of C_2S is distorted via the uptake of external elements (including alkalis, SO_3, P_2O_5, B_2O_3, Fe_2O_3, Cr_2O_3, BaO, V_2O_5 or MgO) or by stabilising high temperature polymorphs. Belite clinkers typically contain 4 wt% to 5 wt% impurities in solid solution (Sark et al. 1981, Chatterjee 1996).

Lafarge in 2006 patented sulfoaluminate belite cements SAB cements activated with 30 % $C_4A_3\check{S}$, in which the belite forms are stabilised by adding borax (sodium tetraborate decahydrate) (Li et all. 2006). Calcium sulfoaluminate cements CSACs, in turn, consist in a blend of $C_4A_3\hat{S}$ (35 % to 70 %), belite and an aluminium-high phase. The behaviour and properties of these belite cements have been studied by Quillin (2001) and Glasser and Zhang (2001), among others, who observed that 1 d CSACs develop strength of 35 MPa to 55 MPa while the values in the 28 d materials amount to 55 MPa to 70 MPa.

A new approach to activating belite (alternative to those explored in the past) is discussed in this paper, which contends that commercial belite cements can be produced with mechanical, setting and other properties that meet the requirements presently in place for commercial cements. The alternative proposed lies within the authors' main lines of research, which have focused on alkaline activation (Palomo et al 2014) and hybrid cement design (García Lodeiro et al. 2013)

2.-MATERIALS, METHODS AND RESULTS

2.1.- Materials

Limestone and slate were used as the primary raw materials to prepare both laboratory and industrial scale belite clinker, with gypsum and fluorite as mineralisers and fluxes (García-Díaz et al. 2011, García-Lodeiro et al 2016). The belite clinker prepared was ground with fly ash and an alkaline activator, a very simple procedure to produce the **hybrid alkaline belite cement that constituted the ultimate objective of this study**. The chemical compositions of the materials used are given in Table 1.

Table 1. Chemical composition of the materials studied (in wt% of oxides)

Material	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	F	L.I.[1]	Other
Limestone	13.1	3.5	1.4	43.2	1.4	0.8	0.9	-	35.3	0.4
Slate	65.3	21.3	2.8	0.1	0.7	0.1	3.9	-	4.7	1.1
Gypsum	19.1	7.6	2.7	20.5	2.8	25.5	1.5	-	19.7[2]	0.6
Fluorite	9.2	0.5	0.4	50.4	0.4	0.5	0.1	27.5	9.7	1.3
Fly ash	51.4	25.8	5.7	4.6	1.5	0.8	1.7	-	6.2	2.3

[1] *Loss on ignition, 100 °C to 1000 °C* [2] *Loss on ignition, 0 °C to 100 °C*

2.2.- Clinker preparation in the laboratory

After characterisation, the aforementioned materials were used to prepare a total of 20 raw belite mixes in the laboratory: 14 without and six with gypsum and fluorite. They were clinkered at 1250 °C to 1350 °C for a constant furnace time of 1 h. All the resulting clinkers were characterised in depth and their hydration was studied. Based on the findings, two mixes were chosen for the rest of the study: one with (**CBm)** and the other without **(CB)** gypsum+fluorite. The two raw mixes chosen were batched as shown in Table 2.

Both were clinkered in an electric furnace. The clinkers obtained were ground and sieved to a particle size of under 45 μm. The free CaO content was found with the ethylenglycol method, while the mineralogical phases were identified with XRD and quantified using the Rietveld method (Table 3).

Table 2. Raw mix batching

Raw mix	Raw material (wt%)			Modulus		
	Limestone	**Slate**		[1]M_F	[2]M_S	[3]LSF
CB	95.9	4.1	-	2.82	2.69	86.75
CBm	**91.1**	**3.9**	**5.0**	**2.82**	**2.69**	**86.75**

[1]$M_F = Al_2O_3 / Fe_2O_3$
[2]$M_S = SiO_2 / (Fe_2O_3 + Al_2O_3)$
[3]$LSF = [CaO / 2.8\ SiO_2 + 1.18\ Al_2O_3 + 0.65\ Fe_2O_3)] \times 100$

Prismatic specimens (1x1x6 cm³) were moulded for the mechanical strength tests. With a view to the ultimate aim of this study, i.e., the preparation of a hybrid alkaline belite cement, blends containing 48 % belite clinker + 48 % fly ash + 4 % gypsum+sodium sulfate were mixed in a laboratory ball grinder. These materials were subsequently hydrated at a liquid/solid ratio of 0.45.

Table 3. Clinkerisation temperature, mineralogical phases and free CaO

Clinker	T(ºC)	Mineralogical phase						Free lime
		C_3S	C_2S	C_3A	[1]$C_{12}A_{7ss}$	C_4AF	$K_2SO_4 \cdot 2CaSO_4$	
KB	1350	32.7	53.1	7.4	-	5.7	--	0.62
KBm	1250	30.2	50.4	0.5	[1]6.3	7.6	---	0.40
KBl		27.1	56.5	2.3	[1]3.4	7.3	1.8	

[1]$C_{12}A_7$ is actually a solid solution of the type $C_{11}A_7 \cdot CaF_2$ (Fluormayenite)

The specimens were chamber cured at 21 ºC and 95 % relative humidity for 24 h, after which they were stored in a climatic chamber until the test age (2 d, 7 d or 28 d). Further to the compressive strength findings shown in Figure 1, the highest values were recorded for the mixes made with mineralised belite clinker.
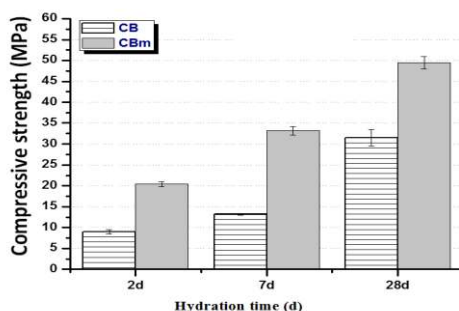

Figure 1.- Paste compressive strength

2.3.- Industrial-scale manufacture of mineralised belite clinker

Mineralised belite clinker KBm was chosen for industrial manufacture. Although initially the laboratory batching was used, namely with the same 0.6 % of CaF_2 in the industrial as in the laboratory raw mix, the fluorite content was subsequently raised at the cement plant to counter the effect of the fuel used to synthesise the clinker, which left a 2.55 % SO_3 residue in the furnace. That measure ensured that all the sulfate present in the furnace would react with the CaF_2 in the raw mx, thereby avoiding the undesirable formation of alkaline sulfates in the furnace and in the clinker.

The XRD- and Rietveld method-determined mineralogical composition of the industrial belite (KBI) and other two clinkers (Table 3) revealed minor compositional differences among them. KBI, for instance, contained a small amount of langbeinite ($K_2SO_4 \cdot 2CaSO_4$) formed in the furnace in keeping with the alkali cycle. Its presence was an indication that the clinkerisation temperature was >1250 °C.

A reflected light optical micrograph of the industrial belite clinker is reproduced in Figure 2, in which the clinker surface was attacked with a 10 vol% solution of nital (HNO_3+ethanol) to better distinguish the phases. The angular crystals (with sharp edges) visible in the figure were identified as C_3S and the granular, irregular crystals with rounded edges as C_2S. The pale coloured, scant interstitial phase comprised C_3A, $C_{12}A_7$ and C_4AF. Belite was more abundant than alite and no free lime was observed, confirming that the product was a low lime saturation belite clinker. Belite morphology denoted slow C_2S clinker cooling [14-15].
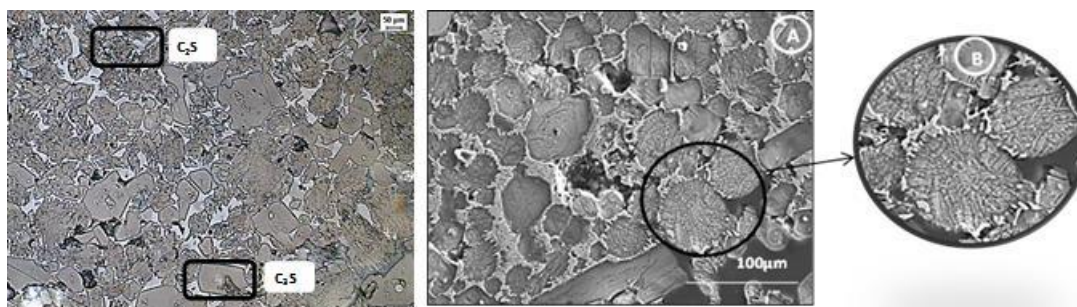

Figure 2.- *Micrographs of industrial belite clinker.*

2.4.- Preparation and physical-mechanical characterisation of hybrid alkaline belite cement

The industrial-scale belite clinker was used to prepare cement with the same composition as established in the laboratory (48 % belite clinker + 48 % fly ash + 4 % gypsum + sodium sulfate, Table 4) was ground with the rest of the components in an industrial ball grinder. Approximately 1000 t of hybrid alkaline belite cement were produced. The 2 d and 28 d mechanical strength values listed in Table 4 were found on prismatic mortar specimens (4x4x16 cm^3) made with this cement at a sand/cement ratio of 3:1 and a water/cement ratio of 0.45. On the grounds of the strength values, the hybrid alkaline belite cement produced in this study would be classified as a European standard EN 197-1 type 32.5N binder.

Table 4. Hybrid alkaline belite cement batching and mechanical strength of mortars.

Blended cement composition				Mortar strength			
KBI	FA	Gypsum	Na$_2$SO$_4$	Flexural		Compressive	
				2 d	28 d	2 d	28 d
48	48	1.5	2.5	3.4±0.15	7.9±0.2	10.8±0.2	39.9±1.14

No significant differences were observed in particle size distribution, setting times or mechanical strength between the hybrid alkaline belite cement and a commercial 32.5N material.

According to the laser-determined particle size and particle size distribution graphed in Figure 3, 96 % of the particles in the hybrid cement had a diameter of under 45 µm, compared to 93 % in the 32.5N commercial product.
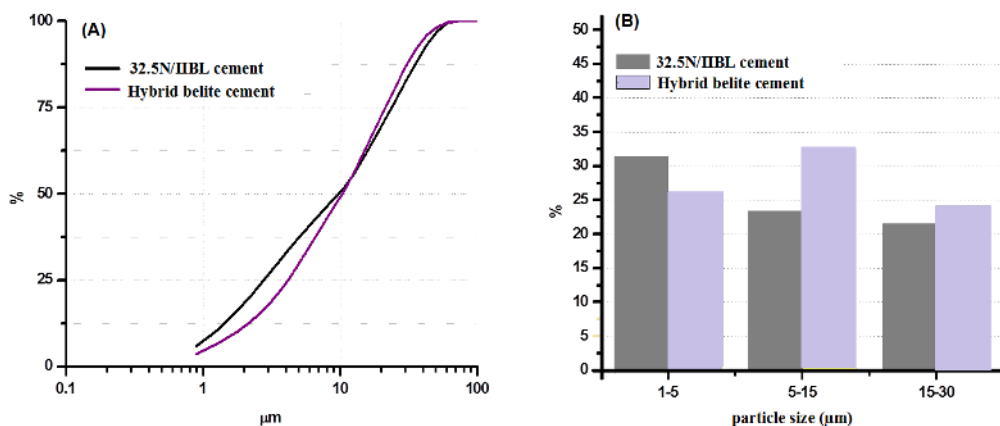

Figure 3.- A) Hybrid and reference cement particle size; B) Hybrid and reference cement particle size distribution

The cement setting times given in Table 5 show that although setting began and ended later in the hybrid than in the reference cement, the former material was European standard EN 196-3-compliant in that respect.

Table 5.- Hybrid and reference cement setting times

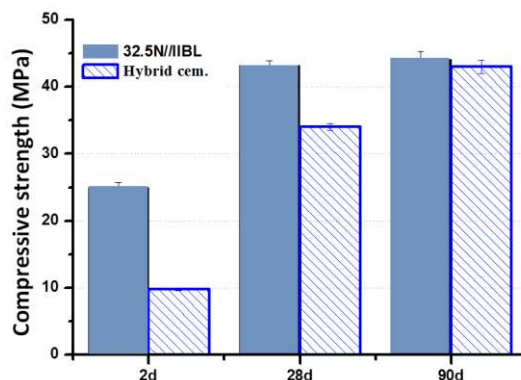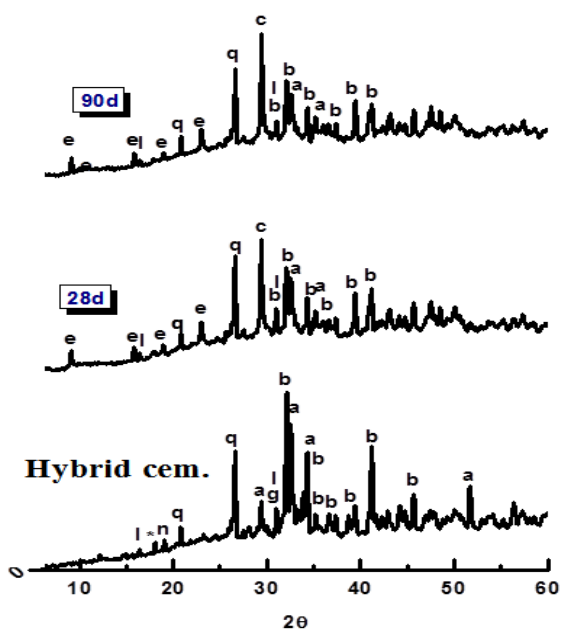| Setting (min)	Standard EN 197-1	Reference 32.5N	Hybrid
Initial	>45	145	215
Final	-	185	377

Figure 4.- Hybrid and reference cement compressive strength

The 2 d, 28 d and 90 d compressive strengths of the alkaline belite and 32.5N cements found on (4x4x16 cm^3) mortar prismatic specimens are compared in Figure 4. Although the hybrid material exhibited lower initial strength than the reference, the 28 d values for both cements were >32.5 MPa. Compressive strength rose much more steeply between 28 d and 90 d in the hybrid than in the reference cement.

2.5.- Hybrid alkaline-belite cement hydration products

After the paste specimens were tested for strength they were crushed to a powder and mixed with acetone and ethanol to detain hydration and prepare the materials for mineralogical and microstructural characterization via XRD BSEM/EDX

*Figure 5.- Diffractograms for anhydrous hybrid cement and its 28 d and 90 d hydrated pastes;(Legend: **b**:C₂S; **a**:C₃S; **q**:quartz; **g**:gypsum; **l**: mullite; **n**:Na₂SO₄; **e**:ettringite; **c**:calcite; *:C₁₂A₇)*

The XRD patterns for the hydrated hybrid cement and the 28 d and 90 d pastes are reproduced in Figure 5. Diffraction lines associated with ettringite and calcite were observed in the diffractograms for the pastes at both ages. The hump observed was associated with the vitreous fraction of fly ash and the presence of one or more cementitious gels. The intensity of the diffraction lines associated with belite was observed to decline steadily with hydration time.

The BSEM/EDX findings for 28 d and 180 d pastes confirmed the precipitation of different types (or mixes) of C-(A)-S-H, N-(C)-A-S-H-like cementitious gels (Figure 6). Due to the interaction between these gels as hydration progressed, the cementitious mix evolved toward the precipitation of a fairly uniform product reminiscent of N,C-A-S-H gel (Qu et al 2016, García-Lodeiro et al. 2011, Walkley et al. 2016).
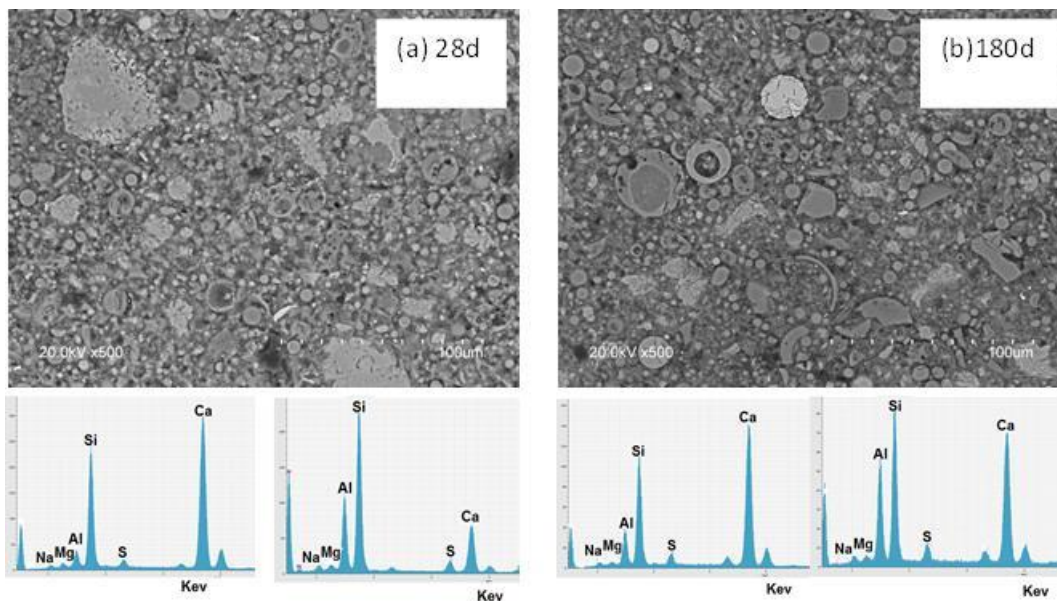
Figure 6.- *BSEM/EDX micrographs of 28 d and 180 d hybrid cement pastes*

3.- CONCLUSIONS

The conclusions that may be drawn from this study are listed below.

- A laboratory-designed mineralised belite clinker was reproduced on an industrial scale with no incidents worthy of note.

- The mineralised belite clinker produced industrially contained 56.5 % C_2S, which optical microscopic analysis showed to constitute type I belite.

- The hybrid alkaline belite cement containing 48 % fly ash prepared met the mechanical strength and setting time requirements laid down in European standard EN 197-1.

- The mechanical strength and setting times of the hybrid alkaline belite cement produced were comparable to those of a standard 32.5N cement.

- Hydration of this hybrid alkaline belite cement favoured the simultaneous precipitation of a mix of cementitious gels that varied in nature: C-(A)-S-H and N-(C)-A-S-H. These gels interacted and over time evolved toward an N,C-A-S-H gel, with no detriment to the mechanical strength developed by the cement.

ACKNOWLEDGMENTS

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