Byproducts use in sulfobelite cements

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Abstract

Today, new building materials, which are produced with lower energy consumption, have low carbon footprint and are environmentally friendly, are increasingly needed. Cement is a major building material, with world production in 3.5 Gt/year, that has helped to develop our cities and culture. A typical total energy requirement for Ordinary Portland Cement (OPC) production is 320-440 MJ/t of cement from the quarry to its packaging and the CO_2 footprint is 900 kg/t of cement. Sulfobelite (SB) cements can be a solution, since they require lower kiln temperature and less CO_2 is emitted during their production, compared to OPC. The main difference of SB from OPC is the appreciable reduction of the phase of alite $(CaO)_3SiO_2$, the increase of the phase of belite $(CaO)_2SiO_2$ and the formation of a new crystalline phase known as yeelemite $(CaO)_4(Al_2O_3)_3SO_3)$ or Klein component. Industrial byproducts, such as FGD (Flue Gas Desulphurisation) gypsum and bauxite residue or alumina refinery residues (ARR), can also be used in their raw meals, decreasing further the CO_2 footprint. All produced compositions were characterized by XRD, Q-XRD, optical microscopy and compressive strength tests were also held. The main conclusion of this study is that the studied industrial byproducts can be used as raw materials for raw meals of cements, accomplishing lower temperatures (1330 ^{o}C), lower CO_2 emissions and significant lower mineral raw materials, combining with comparable strength values. All above conclusions suggest that SB cements can be a promising alternative eco-friendly building material for special uses.

Keywords: sulfobelite, cements, FGD gypsum, Bauxite residue, byproducts, circular economy.

I. INTRODUCTION

Today, the need for reuse, waste recovery, reduced energy consumption and carbon footprint are values that govern the design of every industrial production and are part of circular economy. Cement is a major building material, that has helped to develop our cities and culture, mainly due to its special features combined with its highly competitive price. Cement world production is 3.5 Gt/year, making it an important material for the World Economy. Cement industry is a large energy consumer and a major CO_2 producer (in top 5 industries with highest CO_2 emissions). A typical total energy requirement for Ordinary Portland Cement (OPC) production is 320-440 MJ/t of cement from the quarry to its packaging and the CO_2 footprint is 900 kg/t of cement [1]. This quantity of CO_2 is released into the atmosphere in two ways. Directly, due to decomposition upon heating of $CaCO_3$ ($\rightarrow CaO + CO_2$) found in raw materials (limestone), and indirectly, due to the energy consumption for the production process, mainly for heating furnaces at high clinkering temperatures, 1450 °C [1, 2, 3].

In cement production, four basic oxides, CaO, SiO_2, Al_2O_3 and Fe_2O_3 are needed, which are found in various raw materials and after mixing in suitable proportions, drying and firing at temperatures up to 1450°C a clinker cement is formed. Ordinary Portland Cement (OPC) consist of at least 2/3 of alite $(CaO)_3SiO_2$ and 1/3 of belite $(CaO)_2SiO_2$. Growing early strengths are attributed to the alite phase, while belite contributes mainly to the strengths of the 28^{th} day. The main difference of sulfobelite (SB) from OPC is the appreciable reduction of the phase of alite $(CaO)_3SiO_2$, the increase of the phase of belite $(CaO)_2SiO_2$ and the formation of a new crystalline phase known as yeelemite $(CaO)_4(Al_2O_3)_3SO_3$) or Klein component. Since the production process of cement is particularly energy intensive and damaging to the environment, a promising solution, that does not require changes in the existing production process, is sulfobelite cements for three reasons. First, the production of sulfobelite cements favors the use of byproducts in the raw meal such as FGD gypsum (Flue Gas Desulphurisation gypsum) and bauxite residue (dried red mud, ARR). Second, they require kiln temperatures of 1280-1350 °C, significantly lower than conventional OPC. Third, sulfobelite cements consist of belite $(CaO)_2SiO_2$ and not of alite $(CaO)_3SiO_2$ such as OPC, so less $CaCO_3$ is needed and less CO_2 is produced.

The present study focuses on the production of environmentally friendly sulfobelite cements with byproducts such as FGD gypsum and bauxite residue (ARR), obtained at low burning temperature of 1330 °C.

II. MATERIALS AND METHODS

A. Materials, design and production of SB cements

The raw materials used in this study were limestone, shale, FGD gypsum, bauxite residue (ARR) and Al_2O_3 (99%). Limestone and shale are mineral raw materials which are common in cement production due to their oxide content in CaO, SiO_2, Al_2O_3 and Fe_2O_3. Al_2O_3 (99%) was used to cover any lack of the homonymous oxide existed.

FGD gypsum is a unique synthetic product derived from flue gas desulfurization systems at electric power plants all over the world. SO_2 emission control systems used by coal-fired power plants remove sulfur from combustion gases using calcium compounds and a forced oxidation system produces "FGD gypsum", which is chemically nearly identical to mined natural gypsum filled with SO_2. Electric utilities produce more than 10 Mt of FGD annually and deposite it in specific fields near the plants, causing significant environmental and economic problems [4, 5]. In previous studies of the use of calcium sulphate carriers, FGD has been found to exhibit very encouraging properties as a mineral gypsum substitute as a material in cement [6].

Bauxite residue or alumina refinery residues (ARR), is a highly alkaline byproduct composed mainly of iron oxide that is generated in the industrial production of aluminum. Annually, about 119 Mt of ARR are produced, causing a serious disposal problem in the mining industry. The scale of production makes the byproduct an important one and every opportunity is explored to find uses for it. [7]

All raw materials except FGD were dried at 100 °C (FGD at 60 °C) for 24 h and individually milled in a planetary mill, for proper time at a particle size < 90 μm. Every raw material was analyzed by XRF and the results are shown in Table 1. According to oxide composition of raw materials and modified Bogue equations, sulfobelite cements of three different compositions were prepared in the lab, with 30-50% yeelemite phase ($C_4A_3\hat{S}$) [1]. Every composition of raw meal was calculated by means of an MS Excel worksheet, by regulating the percentage of necessary raw materials for each. (Table 2)

For every composition, the milled materials <90μm were mixed, homogenized with a minimum water addition and formed to pellets of 12-15 mm diameter by hand. Pellets were dehydrated at 100 °C for > 20 h and then fired into a magnesia–chrome refractory crucible with lid, in a Super Kanthal resistance furnace of Nabertherm (Mod HT08/17) at about 3h. To stabilize the a_H- and b-belite mineralogical forms, clinker was cooled rapidly by simultaneous blowing air and crushing by a hammer.

Table 1 XRF analysis and LOI of raw materials

		Concentration (% wt)			
		Limestone	**Shale**	**FGD**	**ARR**
Oxides	SiO_2	6.25	53.76	1.52	8.15
	Al_2O_3	1.23	14.71	0.10	17.30
	Fe_2O_3	0.77	6.72	0.04	38.10
	CaO	50.35	6.47	32.88	11.80
	MgO	0.55	3.35	0.23	0.21
	SO_3	-	0.24	43.00	0.49
	Na_2O	0.10	0.77	-	2.57
	K_2O	0.26	3.48	-	-
	TiO_2	-	-	-	5.76
	Cr_2O_3	-	-	-	0.29
	V_2O_5	-	-	-	0.19
	P_2O_5	-	-	-	0.14
	NiO	-	-	-	0.097
	LOI	41.00	9.00	20.74	7.00
	Sum	100.50	98.51	98.51	92.00

Table 2 Compositions of the produced sulfobelite raw meals

(%) Exp. / Raw Mat.	SB_{30Y}	SB_{40Y}	SB_{50Y}
Lime	56.70	53.20	48.00
Shale	12.40	8.60	7.40
ARR	4.80	5.30	4.10
FGD	17.10	19.20	22.20
Al_2O_3	9.00	13.70	18.30

B. Characterization methods

The obtained clinkers were studied in two forms, in half pieces of pellets and powder at 3800 – 4100 cm^2/g (Blaine). For the determination of mineralogical phases, powdered clinkers were analyzed by XRD (Rigaku). Diffraction patterns were measured in 2θ range of 10–70°, using Cu K_a radiation of 40kV and 30mA, with a 0.01° step size and scan speed 1deg/min. Qualitative analysis was performed by the DIFFRACplus EVA® software (Bruker-AXS) based on the ICDD Powder Diffraction File. Quantitative X-ray diffraction analysis (Q-XRD) was performed using “TOPAS Academic” software (Bruker-AXS). This routine is based on the calculation of a single mineral-phase pattern and the refinement of the pattern using a non-linear least squares routine [8]. A few corrections, including adjustments to the instrument’s geometry, background, sample displacement, detector type and mass absorption coefficients of the refined phases, were applied in order to achieve the optimum pattern fitting.

The half pieces of clinker were incorporated in transparent resin, polished properly with sandpapers, as well as, etched with 1% Nital and observed by optical microscope 1000x METALLOPLAN Leitz with attached DS camera head DS-5M Nikon and Camera control unit DS-L1.

Finally, the characterized milled clinkers were mixed with water and standard silica sand and placed in 40x40x160mm molds. Because the SB clinkers contain a large percentage of anhydride, no gypsum is added for their strength test. All the other procedure was according to Standard EN 196-1:2004 except SB_{30Y}. SB_{30Y} needed 240ml of water instead of 225ml that are written in Standard EN 196-1:2004. The samples were stored at 20 ± 1°C and 90% humidity until the compressive strength tests were held for 2, 7 and 28 days in a TONICOMP III press with loading rate 2400 ± 200 N/s.

III. RESULTS

The main six crystallographic phases determined in SB cements were: alite (C_3S), belite (C_2S), tetra-calcium aluminoferrite (C_4AF), tricalcium aluminate (C_3A), anhydrite ($C\hat{S}$), yeelemite ($C_4A_3\hat{S}$) (where C: CaO, S: SiO_2, A: Al_2O_3, F: Fe_2O_3, $\hat{S}$: SO_3). In Table 3 the compositions of SB cements are presented in two ways: those measured by Q-XRD and those estimated by modified Bogue equations into the brackets [1]. As a result, Q -XRD calculations for mineralogical phases are in accordance with modified Bogue equations.

Table 3 Main crystallographic phases of SB cements by Q-XRD and Bogue predictions (in brackets)

Exp.	%C_3S	%C_2S	%C_4AF	%C_3A	%$C\hat{S}$	%$C_4A_3\hat{S}$
SB_{30y}	4.61 (-)	39.40 (44.95)	15.65 (14.24)	1.77 (-)	3.88 (11.5)	27.01 (29.62)
SB_{40y}	2.59 (-)	28.45 (35.13)	11.73 (13.61)	4.32 (-)	7.74 (10.76)	40.44 (40.83)
SB_{50y}	5.23 (-)	21.95 (26.28)	8,19 (10.94)	5.12 (-)	7,13 (10.87)	51.96 (52.12)

In figures 1-3 are presented, the three SB samples which were observed under optical microscope. The bluer white or dark areas indicate pores of clinker-pellets full of free CaO, the colorful (blue, brown, purple, black) round crystals indicate C_2S, the grey amorphous phases $C_4A_3\hat{S}$ and the white amorphous spots C_4AF [9]. Additionally, the pictures clearly show the difference in the concentration of belite and yeelemite phases of the three SB cement compositions.

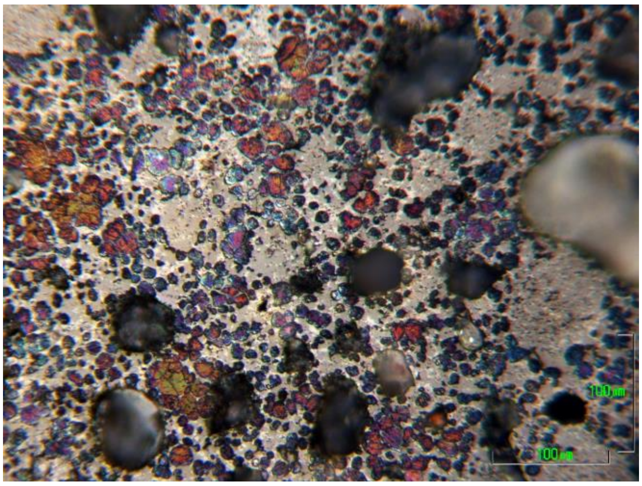

Fig. 1 Image of optical microscopy of SB_{30y}

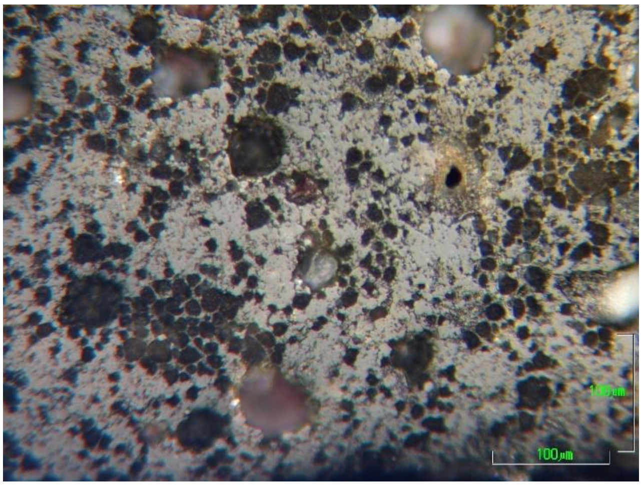

Fig. 2 Image of optical microscopy of SB_{40y}

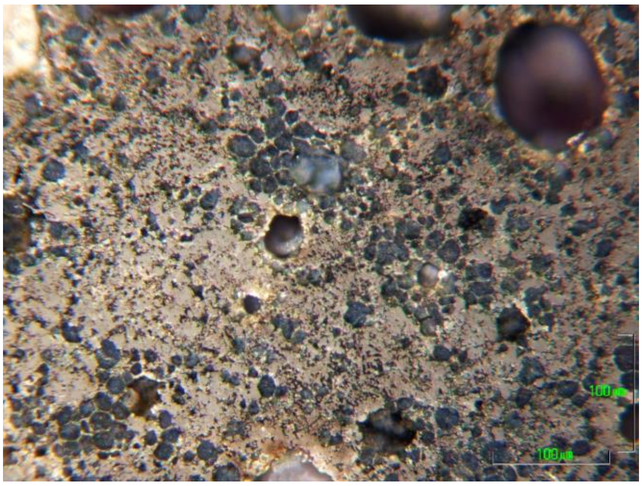

Fig. 3 Image of optical microscopy of SB_{50y}

In Table 4 and Fig 4, are presented the compressive strength results of early, 7th and 28th days for the three SB cement compositions and are compared with OPC CEM32.5N.

Table 4 Compressive strength results of 2, 7 and 28 days. (EN196-1)

Exp.	SB_{30y}	SB_{40y}	SB_{50y}	CEM 32.5N
(Days)		(MPa)		
2	21.3	16.6	43.9	-
7	25.2	13.8	38.0	>16
28	36.6	21.9	30.4	32.5-52.5

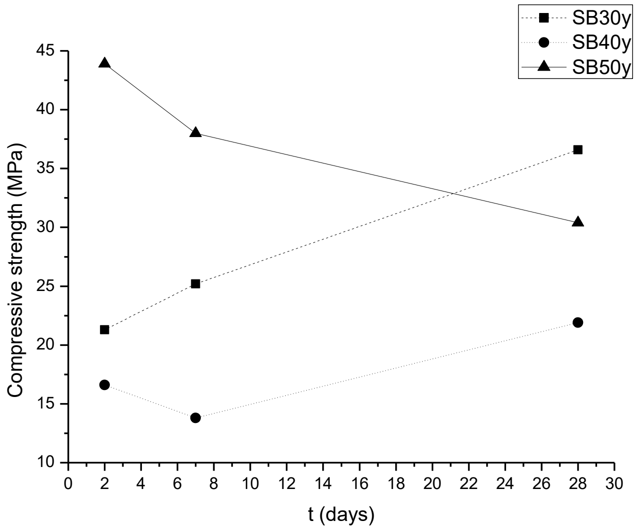

Fig4 Compressive strength results for 2, 7 and 28 days

IV. Conclusions

The main conclusions of this study are:

- Industrial byproducts, such as FGD gypsum and ARR, can be used as raw materials for raw meals of cements.
- Mineral raw materials consumption is significantly reduced in raw meal compared to the percentage of OPC.
- SB Cements can be obtained in lower temperatures (1330 °C), reducing energy consumption.
- CO_2 emissions can be reduced due to lower lime quantity used and lower energy requirements.
- Q -XRD calculations for mineralogical phases are in accordance with modified Bogue equations.
- All SB compositions present better 7th days strength than OPC cements.
- Increase of percentage of yeelemite and simultaneous decrease of belite in SB compositions doesn't affect proportionally the compressive strength values.

- In SB_{50y} composition, which has more yeelemite and less belite, there is a decrease in late strength and that phenomenon is under study.

All above conclusions suggest that SB cements can be a promising alternative eco-friendly building material for special uses.

V. Acknowledgments

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- TITAN Cement Company SA for raw materials supply, as well as XRF and XRD analysis.

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