

## **Synthesis and characterization of belite calcium sulfoaluminate cements produced by oxyfuel combustion residues**

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### **ABSTRACT**

In this work, the possibility of reusing ashes issued by an oxyfuel combustion process (OC) as a source of material in the production of belite calcium sulfoaluminate BCSA cements has been investigated. OF process is one of the most promising combustion technologies for CO<sub>2</sub> reduction from power plants. Combustion tests were carried out in an oxyfuel bubbling fluidized bed pilot plant. Four BCSA clinker-generating raw mixes were heated in a laboratory electric oven in the temperatures range 1150°-1350°C: one included only natural materials (limestone, clay, bauxite and gypsum), the others contained OC ashes as total substitute for clay.

X-ray diffraction (XRD) analysis on the burning products showed high conversion of reactants toward the main BCSA clinker components (C<sub>2</sub>S and C<sub>4</sub>A<sub>3</sub>), especially at 1200° or 1250°C. Moreover, physical-mechanical tests associated with XRD and differential thermal-thermogravimetric analyses accomplished on all the cements (obtained by adding natural gypsum to the clinkers produced at the best synthesis temperatures) generally displayed a similar hydration behaviour.

**Keywords:** Oxyfuel combustion residues, clinker, belite calcium sulfoaluminate.

### **INTRODUCTION**

The rapid growth of World population, the energy demand increase, the global warming (GW) have pushed governments and international authorities to set on the path towards sustainable development. There is no doubt that GW represents the most significant challenge to achieving sustainable development; this phenomenon is caused by the emission and accumulation in the atmosphere of greenhouse gases

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(GHGs) which are mainly released by the burning of fossil fuels, land clearing, agriculture-related and other human activities [Benhelal et al., 2013; De Richter et al., 2016; Szulejko et al., 2017; Telesca et al., 2017]. Carbon dioxide is blamed to be the main responsible for GW; therefore, searching for promising approaches to mitigate CO<sub>2</sub> emissions represents the priority of studies aimed at alleviating the threat of climate change. In this regard, the carbon capture and storage (CCS) technology has the potential to almost completely eliminate CO<sub>2</sub> [Boot-Handford et al., 2014; Leung et al., 2014; Telesca et al., 2014a; Telesca et al., 2017]. CCS indicates a group of technologies developed to obtain CO<sub>2</sub>-rich flue gases ready to be stored by injection into geological strata with specific features. Among the different CCS processes (e.g., chemical absorption, chemical and calcium looping), oxyfuel combustion (OC) is of great interest due to its conceptual simplicity [Diez et al., 2015]. In OC a blend of nearly pure oxygen and part of exhaust gas (employed as O<sub>2</sub> diluent for safety reasons), is used for combustion, thus lowering both N<sub>2</sub> and NO<sub>x</sub> contents in the exhaust gas [Buhre et al., 2005; Lupiáñez et al., 2013a; Lupiáñez et al., 2014]. In absence of the most relevant diluent for CO<sub>2</sub> and after further treatments, it is possible to obtain streams >90% CO<sub>2</sub>-rich. The CO<sub>2</sub>-rich stream is thus ready for final processing and geological storage.

Cement production is one of the most large-scale raw materials consuming as well as energy-intensive manufacturing processes and represents one of the major industrial sectors giving rise to CO<sub>2</sub> emission. In fact, the World's annual cement production currently accounts for about 4.7 billion tons [Activity report 2016, 2017] and its contribution to the global anthropogenic CO<sub>2</sub> emission is estimated as high as 7% (about 26% of the industrial CO<sub>2</sub> emission) [Tregambi et al., 2018]. It is therefore widely accepted the need to increase the sustainability of cement mainly oriented at mitigating the CO<sub>2</sub> impact.

Portland cement (PC) is the most widely used binder all over the World; it is obtained by intergrinding PC clinker (PCC) with a few percent of calcium sulfates (mostly gypsum). For each kg of PCC produced, about 0.87 kg of CO<sub>2</sub> are released [Barcelo et al., 2014]; carbon dioxide comes from both limestone thermal decomposition (about 60% of the total CO<sub>2</sub> emission) and fuel combustion. Therefore, one approach to lower CO<sub>2</sub> emissions is related to the limestone reduction in the clinker-generating raw meal [Telesca et al., 2016]. In this regard, belite rich-cements are considered environmentally friendly binders inasmuch as they can allow a CO<sub>2</sub> reduction as much as 10% [Pimraksa et al., 2009; Cuberos et al., 2010]; moreover, the presence of calcium sulfoaluminate (C<sub>4</sub>A<sub>3</sub>S) in the cement clinker can both compensate the lower reactivity of belite (relative to alite) and further reduce the limestone requirement in the raw feed [Quillin, 2001]. Belite calcium sulfoaluminate (BCSA) cements generally display physical and mechanical properties comparable to OPC [Selçuk et al., 2010]; in fact, their technical behaviour mostly depends on the ability of C<sub>4</sub>A<sub>3</sub>S and C<sub>2</sub>S, to respectively generate, upon hydration, C<sub>6</sub>A<sub>3</sub>H<sub>32</sub>, ettringite (at early ages) and CSH (at medium and longer ages). Moreover, BCSA cements are interesting hydraulic binders from the environmental point of view inasmuch as their manufacturing process, compared to that of OPC, displays a pronounced environmentally friendly character mainly associated to (a) the relatively low synthesis temperature, (b) the decreased specific fuel consumption [Marroccoli et al., 2010a], (c) the easier

grindability and (d) the greater usability of industrial wastes and by-products whose utilization is generally complicated [Marroccoli et al., 2009; Marroccoli et al., 2010b; Ma et al., 2014; Shen and Qian, 2015]. BCSA cements are generally produced by burning a raw mix composed by limestone (L), bauxite (B), clay (C) and gypsum (G) at temperatures ranging from 1250°-1350°C [Xue et al., 2016].

In this paper, residues generated during an OC process, carried out in a pilot-scale fluidized bed (FB) reactor, were tested as substitutes for clay in the BCSA clinker-generating raw mix.

Four mixtures were heated in a laboratory electric oven in the temperatures range 1150°-1350°C: one included only natural materials (taken as a reference term), the others contained OC residues in a measure comprised between 24.5 and 56.0% by mass. The conversion of reactants towards  $C_2S$  and  $C_4A_3S$  was investigated by means of X-ray diffraction (XRD) analysis. XRD and differential thermal–thermogravimetric (DT–TG) analyses together with physical and mechanical tests were employed as main characterization techniques to carry out the investigation.

## EXPERIMENTAL

### Materials and Oxyfuel Pilot Plant

The natural materials (L, C, B and G) used in this investigation were taken from quarries located in Italy. The OC ashes came from a 95 kW<sub>th</sub> pilot-scale bubbling oxyfuel fluidized bed (FB) reactor (2.5 m high with an inner diameter of 21 cm); it is schematically reported in Figure 1 and described elsewhere [Lupiáñez et al., 2013b].

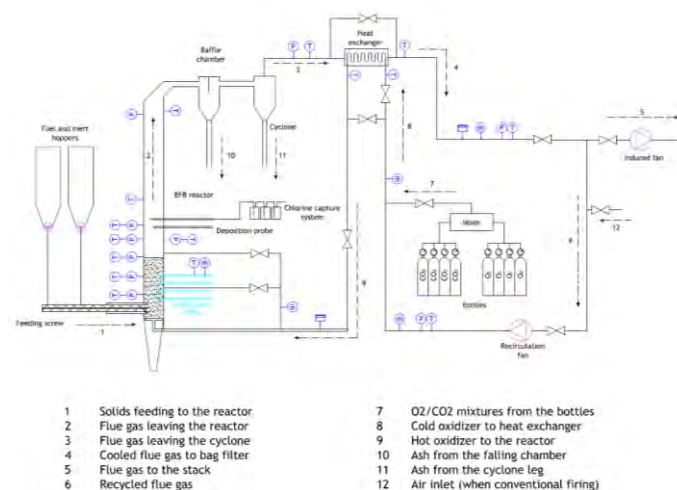


Figure 1. Oxyfuel fluidized bed pilot plant.

The FB reactor (R), cooled by means of a water jacket placed at its bottom and four water-cooled probes uniformly distributed, was charged with a bed inventory of 5 kg silica sand, fluidized at 0.8 ms<sup>-1</sup> (with a 65% CO<sub>2</sub>–35% O<sub>2</sub> mixture) and heated up to 850°C or 925°C; it was equipped with two different devices for the removal of fly ash (baffle chamber, BC, and cyclone, CY, in the order) from the flue gas stream.

A blend of lignite and biomass corn stover fed the apparatus in a 70:30 energy ratio;

moreover, to capture the SO<sub>2</sub> generated during the combustion through the *in situ* desulfurization (calcium, Ca (in the sorbent): sulfur, S (in the fuel)), two different limestones (A and B) were alternatively injected into FBR.

Three different tests were performed: their operating conditions, for the sake of clarity, are summarized in Table 1. During each test, three kind of combustion residues were collected: a bottom ash (BA), extracted from the bottom of FBR, and two fly ashes (BCFA, CYFA) withdrawn along the flue gas treatment line.

Table 1. Operating conditions of the tests carried out in the in the FBR.

Test no.	Fuel	Limestone	Ca:S	FBR Temperature, °C
1	Lignite+Corn stover	A	2	925
2	“	A	6	850
3	“	B	6	925

The residues of each test were then mixed to prepare three blends (B1, B2 and B3), proportioned consistent with the corresponding amount generated during the experimental activity (40%BA-50%BCFA-10%CYFA).

The chemical composition (in terms of major oxides) of the raw materials, determined by X-ray fluorescence technique (wavelength dispersive BRUKER Explorer S4 apparatus), is shown in Table 2.

Table 2. Chemical analysis of the natural and waste raw materials, wt%

	L	B	G	C	B1	B2	B3
CaO	55.16	-	30.10	10.40	49.92	27.13	16.84
SiO <sub>2</sub>	-	7.20	3.00	54.10	21.35	37.70	44.38
Al <sub>2</sub> O <sub>3</sub>	-	56.30	0.90	11.50	4.23	8.62	10.67
Fe <sub>2</sub> O <sub>3</sub>	-	6.30	0.30	4.50	3.86	10.54	11.63
SO <sub>3</sub>	-	-	36.20	-	7.26	6.87	5.51
Others	-	2.30	3.70	6.40	1.89	3.28	2.97
L.o.i.*	43.40	27.50	24.60	13.10	11.48	5.85	8.00

\*Loss on ignition at 950°C

### Mixtures Design and Cements Preparation

Four BCSA clinker-generating raw mixtures were designed according to the modified Bogue equations [Irvin et al., 2011], assuming that C<sub>2</sub>S, C<sub>4</sub>A<sub>3</sub>\$, C<sub>4</sub>AF and C\$ amount fell in the range 45%-60%, 20%-30%, 8%-20% and 4%-10%, respectively; moreover, a free CaO concentration value lower than 1.5% was also considered. All the mixtures contained L, B and G; a reference mix (MR) included also clay (C), whereas the remaining three mixtures (M1, M2 and M3) alternately contained B1, B2 or B3 as total substitute for C. Table 3 and 4 respectively report the modified Bogue potential mineralogical composition of the four clinkers (CLIR, CLI1, CLI2 and CLI3) and the raw meals proportion.

Table 3. Bogue potential mineralogical composition of the clinkers, wt%

	C <sub>2</sub> S	C <sub>4</sub> A <sub>3</sub> \$	C <sub>4</sub> AF	C\$	C
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CLIR	56.0	25.9	8.3	5.1	0.1
CLII	48.7	23.9	12.4	9.7	1.4
CLI2	52.6	20.7	17.9	4.9	0.1
CLI3	50.2	22.8	16.4	7.1	0.1

The raw mixtures were heated in covered platinum crucibles in a laboratory electric oven for two hours at 1200°, 1250°, 1300° and 1350°C and then rapidly cooled to room temperature; the obtained BCSA clinkers were finely ground in a Fritsch Pulverisette 6 (FP6) laboratory planetary mill to pass a 90 µm sieve and afterwards submitted to XRD analysis in order to assess the best temperature for maximizing both C<sub>2</sub>S and C<sub>4</sub>A<sub>3</sub>S concentration.

Table 4. Composition of the raw meals, wt%

	L	B	G	C	B1	B2	B3
MR	53.0	13.0	12.0	22.0	-	-	-
M1	50.0	13.0	5.0	-	56.0	-	-
M2	20.0	16.0	8.0	-	-	32.0	-
M3	52.0	13.5	10.0	-	-	-	24.5

BCSA cements (CEMR, CEM1, CEM2 and CEM3) were then prepared by grinding the best obtained clinkers with G in the FP6 laboratory mill always to pass the 90 µm sieve. The amount of the added gypsum was determined considering both the C<sub>2</sub>S already present in the clinker (calculated with the modified Bogue equation) and the reaction stoichiometry for the generation of ettringite (C<sub>6</sub>A<sub>3</sub>H<sub>32</sub>, the main hydration product regulating the technical behavior at early ages) and aluminium hydroxide (AH<sub>3</sub>) [Manzano et al., 2012; Telesca et al., 2014c], namely:



XRD analysis was also employed for the evaluation of BCSA cements hydration products; it was performed with a Bruker D2 Phaser diffractometer (CuK $\alpha$  radiation and 0.02°2 $\theta$ s<sup>-1</sup> scanning rate).

### Measurements on Mortars

BCSA mortar prisms were prepared according to the European Standard EN 196-1 and cured after demolding under water at 20°±1°C; they were submitted to compressive strength measurements at curing periods ranging from 1 to 56 days.

### Measurements on Pastes

BCSA cements were paste hydrated with a water/cement ratio equal to 0.5 by mass. The paste samples were cast into 15-mm-high and 30-mm-diameter cylindrical molds, and finally placed in polyethylene bags inside a thermostatic bath (at 20°C and 95% relative humidity) for curing times ranging from 4 hours to 56 days. At the end of each aging period the specimens were first crushed and then treated with acetone (to stop hydration) and diethyl ether (to remove water); the pulverized samples were subsequently stored in a desiccator over silica gel–soda lime (to ensure protection

against H<sub>2</sub>O and CO<sub>2</sub>) and finally submitted to simultaneous DT-TG (NETZSCH-Tasc 414/3 apparatus, heating rate 10°C min<sup>-1</sup>, operating between room temperature and 1000°C) and XRD analyses.

For the expansion–shrinkage measurements, eight paste samples, shaped as small prisms (15X15X78 mm), were first air cured at 20°C for 4 hours and then demolded. Later on, one set of samples was aged at 20°C under tap water, the other stored in a controlled humidity (H) chamber at 70% R.H. and 20°C. The length changes were determined as average values of four measurements with a caliper accurate to ±1 μm; the reference length for them was that evaluated just after demolding [Telesca et al., 2014b; Valenti et al., 2012].

## RESULTS AND DISCUSSION

The intensity of the main XRD peaks of C<sub>2</sub>S and C<sub>4</sub>A<sub>3</sub>S were taken as a conversion index of the BCSA clinker-generating raw mixes toward these products. The “external standard method” [Cullity et al., 2001] was used and, as a reference line, the same reflection from pure C<sub>2</sub>S and C<sub>4</sub>A<sub>3</sub>S preparations (generated by high-temperature synthesis of analytical grade calcium carbonate and quartz for the former and calcium carbonate, alumina and gypsum for the latter) was taken [Telesca et al., 2015]. The XRD intensity (cps) of the C<sub>2</sub>S and C<sub>4</sub>A<sub>3</sub>S lines is plotted as a function of the heating temperature (Figure 2 (a) and 2 (b), respectively); each curve displays a maximum occurring, for C<sub>2</sub>S, at about 1200 °C (MR and M2) or 1250°C (M1 and M3). Concerning calcium sulfoaluminate, the best synthesis temperature was the same as that of belite for mixtures M1 and M2, while higher for MR (1250°C) and M3 (1300°C).

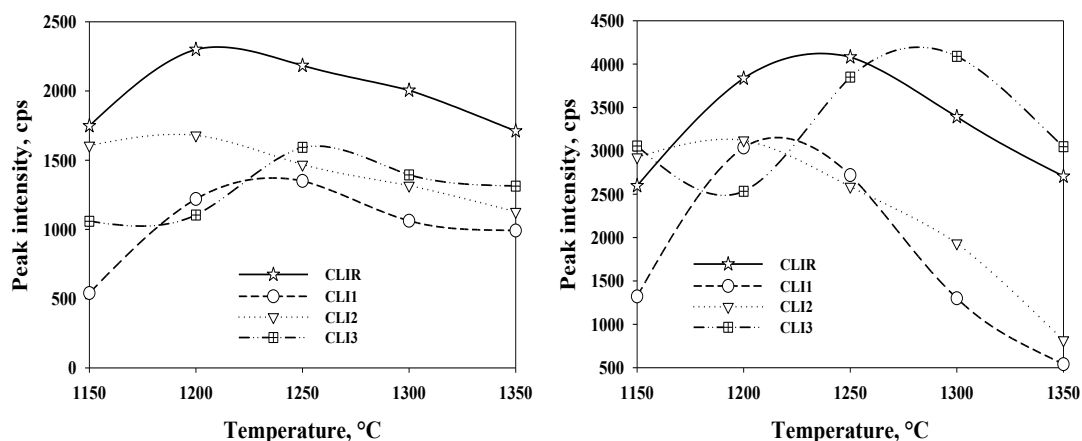


Figure 2. XRD intensity (counts per second, cps) of the C<sub>2</sub>S and C<sub>4</sub>A<sub>3</sub>S main peak for the BCSA clinkers as a function of the synthesis temperature.

From an overall examination of the XRD data about the synthetic BCSA clinkers it was found that, at every investigated temperature, the conversion of reactants was complete and C<sub>2</sub>S and C<sub>4</sub>A<sub>3</sub>S were the main burning products. Furthermore, C<sub>4</sub>AF, C<sub>2</sub>AS and C\$ frequently occurred as secondary components.

Figure 3 illustrates the XRD patterns of mixtures MR, M1, M2 and M3 heated at the best synthesis temperatures. The four BCSA cements obtained from the synthetic clinkers generated by RM, M1, M2 and M3 at their best synthesis temperature were respectively denoted with the symbols CEMR, CEM1, CEM2 and CEM3.

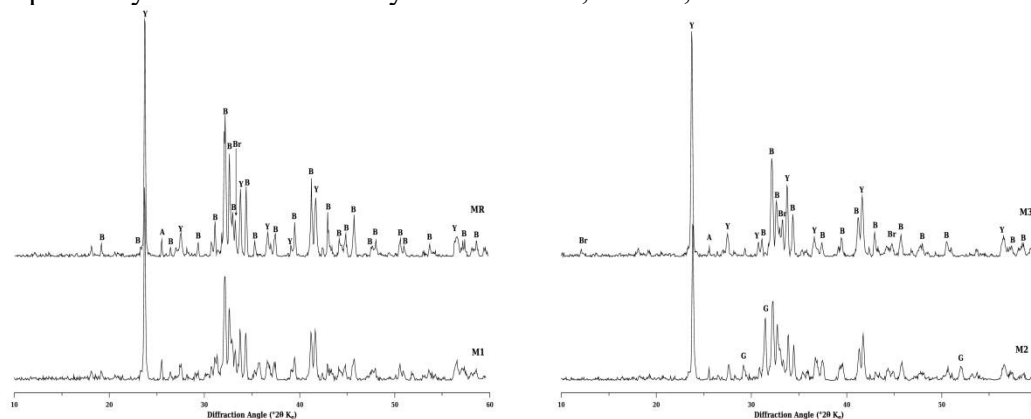


Figure 3. XRD patterns for the BCSA clinkers obtained from MR, M1, M2 and M3 at their best synthesis temperature. Legend to symbols: Y=C<sub>4</sub>A<sub>3</sub>S, A=C<sub>3</sub>S, B=C<sub>2</sub>S, G=C<sub>2</sub>AS, Br=C<sub>4</sub>AF.

Table 5 reports the compressive strength development of BCSA-based mortars as a function of curing time; at all the investigated periods, the compressive strength values of CEMR, CEM2 and CEM3 based-mortars were similar to each other; on the contrary, the compressive strength values of CEM1 were constantly lower than those of the other cements.

Table 5. Results of compressive strength measurements of CEMR, CEM1, CEM2 and CEM3 at various aging periods.

Days	CEMR	CEM1	CEM2	CEM3
1	12.7±0.4	8.7±0.5	10.9±0.3	12.2±0.3
2	19.2±0.3	14.5±0.2	16.1±0.5	19.7±0.2
7	26.4±0.2	20.4±0.6	24.5±0.5	27.9±0.5
14	32.5±0.1	24.6±0.3	30.5±0.8	33.5±0.2
28	37.1±0.5	26.9±0.1	34.5±0.7	36.8±0.4
56	36.9±0.7	28.4±0.5	35.1±0.8	37.1±0.3

The compressive strength results refer to three prisms (six determinations)

The results of the expansion–shrinkage tests are illustrated in Figure 4.

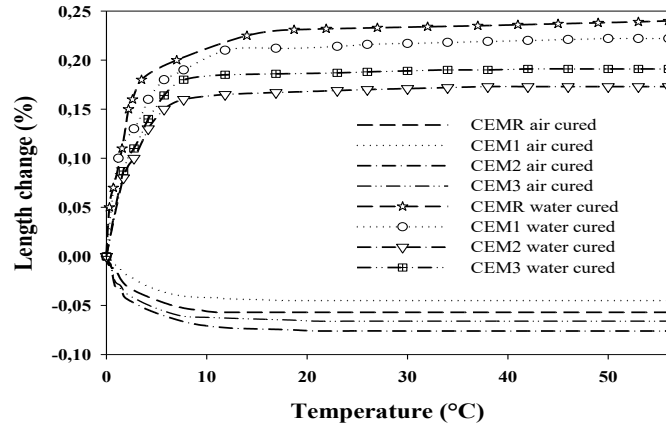


Figure 4: Dimensional stability curves for BCSA-based cements (air and water cured). They indicate that all the investigated BCSA cements differed very little from each other, both when submerged under water and cured in air. In particular, under water the maximum expansion values, reached after about 14 days of curing, are comprised in the narrow range of 0.17-0.23%. When cured in air, the investigated pastes showed a continuous shrinkage till 14 days when a minimum length change is reached (-0.06%, -0.05%, -0.08 and -0.07% for CEMR, CEM1, CEM2 and CEM3, respectively); since that period the values remained constant for all the investigated systems.

The change of mineralogical phases with ongoing hydration was determined through XRD and DT-TG investigations. The XRD analysis of all the BCSA cements revealed, as expected, that after 4 hours of hydration ettringite had already formed at the expense of part of calcium sulfoaluminate and calcium sulfates. At 28 days of curing ettringite was still the main crystalline phase of hydrated cements which also revealed the presence of some traces of  $C_4A_3S$  and inert phases (e.g. gehlenite). At the same curing period, strätlingite ( $C_2ASH_8$ ), which started forming already after 1 day of curing in CEMR and CEM1, was evident together with katoite ( $C_3AH_6$ ) in all the investigated systems. These compounds had respectively formed from belite (as silicon source) and  $AH_3$  (as aluminium source) and from the remaining belite and  $C_2ASH_8$  according to the following equations [Winnefeld et al., 2016]:



Moreover,  $AH_3$  was not detected at any curing period due to its amorphous nature. No significant changes were observed at 56 days of curing in the four hydrated systems. As an example, XRD patterns for CEMR, CEM1 and CEM3 hydrated at 4 hours, 1 and 56 days are reported in Figure 5.



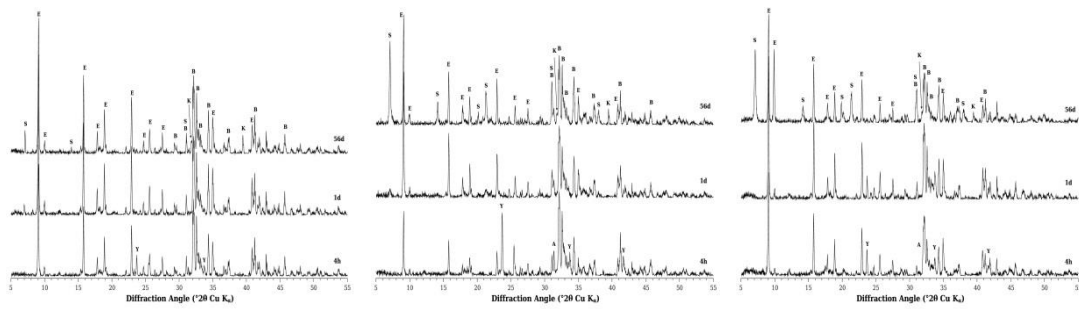
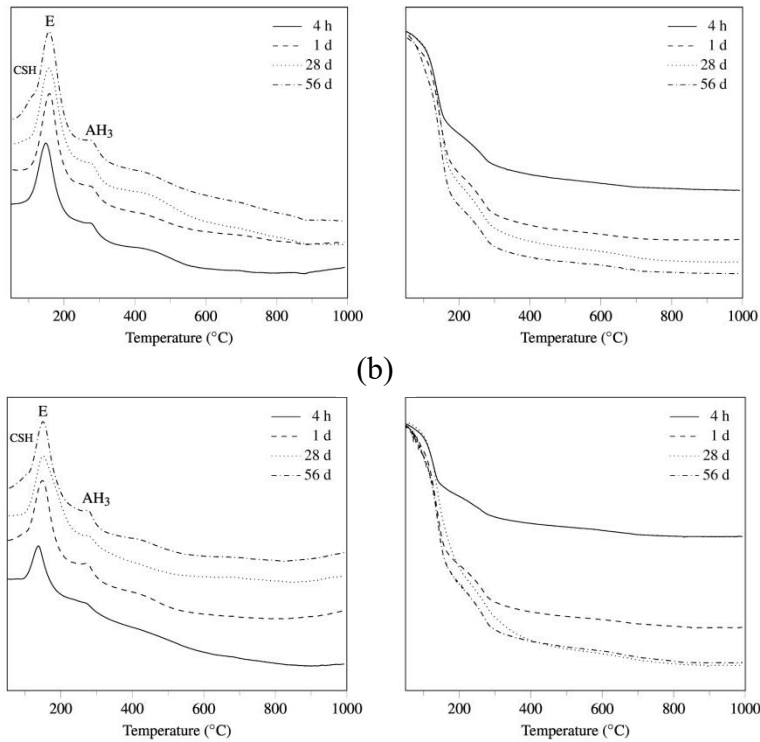


Figure 5. XRD patterns for CEMR (left), CEM1 (middle) and CEM3 (right) hydrated for 4 hours, 1 and 56 days. Legend to symbols: E=C<sub>6</sub>A<sub>3</sub>H<sub>32</sub>, Y=C<sub>4</sub>A<sub>3</sub>S, S=C<sub>2</sub>ASH<sub>8</sub>, K=C<sub>3</sub>AH<sub>6</sub>, B=C<sub>2</sub>S.

The DT–TG analyses almost confirmed the mineralogical evaluations made by XRD. Three endothermic effects were observed and attributed, on the basis of literature data [Taylor, 1997], to the following compounds: ettringite (E) and, contrary to XRD data, calcium silicate hydrate (CSH) and aluminum hydroxide (AH<sub>3</sub>); in particular, CSH, E and AH<sub>3</sub> were respectively detected through the following dehydration endothermic peaks: 103°±4 °C, 152°±5°C, 277°±3°C. Strätlingite could not be identified inasmuch as its DT peak was overlapped by the ettringite one.



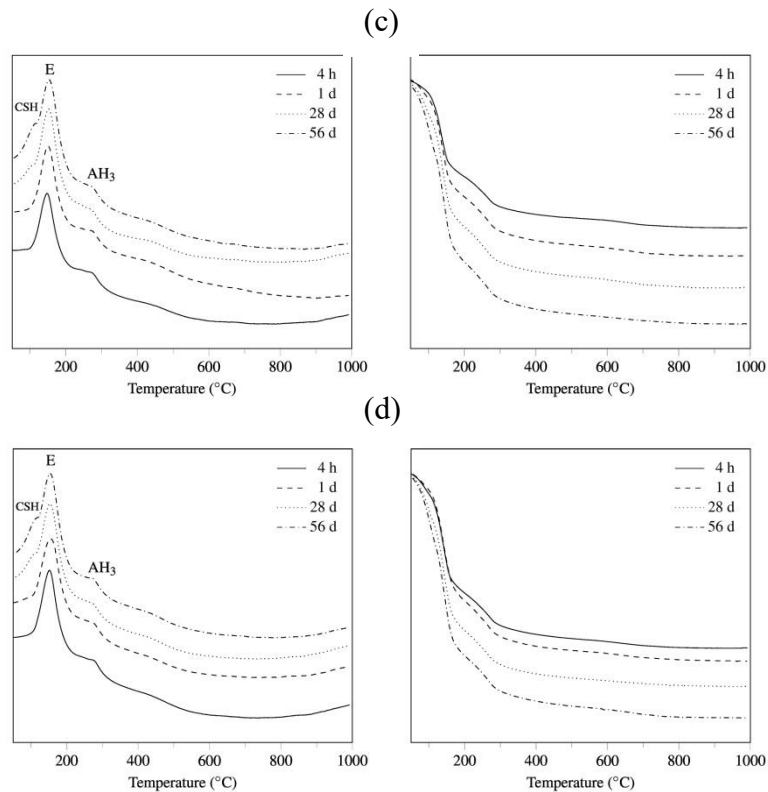


Figure 6: DT-TG thermograms for BCSAR (a), BCSA1 (b), BCSA2 (c) and BCSA3 (d), hydrated for 4 hours, 1, 28 and 56 days. Legend to symbols: CSH=calcium silicate hydrate; E=ettringite; AH=aluminium hydroxide.

CSH originated from the reaction between belite and strätlingite according to reaction (3); ettringite and aluminum hydroxide represented the main reaction products of  $C_4A_3S$  hydration (equation 1). From the examination of the DT-TG results (Figure 6), it can be drawn that: (a) the thermograms for all the BCSA cements are qualitatively similar; (b) the peak intensities for E and  $AH_3$  generally increase with the increase in the curing time; (c) the presence of CSH is evident starting from 28 days of curing for CEMR, CEM2 and CEM3, only from 56 days for CEM1.

## CONCLUSIONS

The OC residues, generated in an oxyfuel combustion plant, represent a suitable substitute for clay as a silico-aluminous source in belite calcium sulfoaluminate (BCSA) clinker-generating raw mixes. Therefore, the well-recognized environmentally friendly character of the BCSA cement manufacture can be further improved by using industrial wastes and by-products instead of natural materials. It has been found that three different waste-based mixes, laboratory heated at 1200° or 1250°C were able to give, like the reference mix containing only natural materials, high conversion of reactants and good selectivity toward the main BCSA cement components ( $C_2S$  and  $C_4A_3S$ ). The XRD and DT-TG analyses carried out for investigating the hydration behaviour of the BCSA cements, demonstrated that no significant differences associated with the kind of the clayish source were found.

Because of the strong dependence of the cement technical performance on its hydration characteristics, it can be argued that the similarity in the hydraulic behavior among the investigated cements most likely results in analogous engineering properties; this was confirmed by the expansion/shrinkage measurements as well as mechanical compressive strength results.

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