CHEMICAL ENGINEERING TRANSACTIONS
VOL. 86, 2021
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it
Guest Editors: Sauro Pierucci, Jiří Jaromír Klemeš

ISBN 978-88-95608-84-6; **ISSN** 2283-9216

Production of Eco-Friendly Blended Calcium Sulfoaluminate Cements by Using Biomass-Fly Ashes

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The manufacture of Ordinary Portland cement (OPC) generates about 8% of all anthropogenic CO_2 emissions; therefore, carbon dioxide footprint reduction represents the main challenge for the cement industry. The development of environmentally friendly binders, as alternative to OPC, absolutely represents an efficient way to cut carbon emissions. In this regard, during the last twenty years particular attention has been paid to calcium sulfoaluminate (CSA) cements thanks to their valuable technical properties as well as the environmentally friendly features mainly related to their manufacturing process. In addition, a further reduction in carbon dioxide emissions can be achieved diluting CSA cements with supplementary cementitious materials (SCMs) such as industrial wastes. In this title, biomass fly ashes (BFAs) were used as SCMs in CSA-blended cements; BFAs were preliminarily washed (W_BFAs) in order to lower their content in alkali. The influence of the ashes on both hydration properties and technical behaviour of two CSA blended cements, respectively containing 10% and 20% by mass of W_BFAs, was investigated by means of mechanical compressive strength and dimensional stability measurements associated with X-ray diffraction, differential thermal-thermogravimetric and mercury intrusion porosimetric analyses.

1. Introduction

In 2019 global cement production was about 4.1 billion tonnes; in the same year the total carbon dioxide generated by cement plants reached almost 3.0 billion tonnes, accounting for nearly 8% of all anthropogenic CO_2 emissions (IEA, 2020, Tregambi et al. 2018). Therefore, the main challenge for the cement industry is to curb its carbon footprint; to this end, both cement producers and scientific community have suggested several solutions, such as: a) a larger utilization of alternative fuels; b) the application of carbon capture and storage technologies to cement plants and c) the development of alternative eco-friendly binders (EFBs) (Telesca et al., 2016); EFBs can be produced following three different approaches, namely I) the use of a non-carbonated CaO source instead of limestone as a constituent of the raw mixture for the generation of the burnt product (cement clinker); II) the increased production of blended cements, obtained by adding significant amounts of supplementary cementitious materials (SCMs) (Telesca et al., 2017) to traditional ordinary Portland cements (OPCs); III) a greater utilization of special binders (e.g. Mg-based cements, alkali-activated, calcium sulfoaluminate (CSA) and belite-CSA (BCSA) binders) (Luukkonen et al., 2018; Telesca et al., 2020; Walling and Provis, 2016).
CSA cements have attracted the interest of the international cement community thanks to their valuable technical properties as well as the eco-friendly features of their manufacturing process (Gartner et al., 2015; Marroccoli et al., 2009; Marroccoli et al., 2010a; Marroccoli et al., 2010b; Telesca et al., 2016; Telesca et al., 2019a; Telesca et al., 2019b). $3CaO{\cdot}3Al_2O_3{\cdot}CaSO_4$ is the main mineralogical component of CSA cements; furthermore, they can also contain calcium sulfates, $2CaO{\cdot}SiO_2$, $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$, $4CaO{\cdot}2SiO_2{\cdot}CaSO_4$ and various calcium aluminates, depending on the synthesis temperature as well as type and proportioning of raw materials. The CSA technical properties (e.g. rapid setting, high early strength, shrinkage compensation/self-stressing behaviour, good dimensional stability, elevated impermeability,) mainly depend on the formation of ettringite ($3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$) which forms through the hydration of $CaSO_4$ (belonging and/or added

to CSA clinker) with $3CaO{\cdot}3Al_2O_3{\cdot}CaSO_4$ (Chen et al., 2012; Glasser and Zhang, 2001; Winnefeld and Lothenbach, 2010; Marroccoli et al., 2007). In addition, compared to OPC, the manufacturing process of CSA cements occurs at lower synthesis temperatures (<1350°C) and requires a reduced limestone amount (<40%); consequently, fewer fossil fuels are consumed and CO_2 emissions are reduced. In order to further lower the carbon footprint and cut the high costs of production (largely depending on the use of bauxite in the generating raw meal), CSA cements can be mixed with proper SCMs (Garcia-Mate et al., 2013; Lukas et al., 2017; Martin et al., 2015; Pelletier-Chaignat et al., 2012). The addition of biomass fly ashes (BFAs) to OPC has been documented in several scientific articles (Berra et al., 2015; Rajamma R.J.B. R. 2009; Rajamma et al., 2015; Siddique, R., 2012; Tosti et al., 2018). BFAs usually come out from the combustion process of wood, agriculture wastes and herbaceous biomass in thermal power plants. The chemical and mineralogical composition of BFAs depend on the biomass characteristics as well as the combustion technology; they are generally landfilled (van Eijk et al., 2012) or used in forest agricultural fields (Kwapinski et al., 2010) owing to their high alkali content.
This paper aimed to investigate the use of BFAs, formerly submitted to an alkali reduction treatment by means of a water-washing process (WWP), as SCMs in CSA blended-cements; these binders were submitted to physical-mechanical and hydration tests for aging periods comprised in the range 4 hours - 56 days. X-ray diffraction (XRD) and differential-thermal thermogravimetric (DT-TG) analyses coupled with mercury intrusion porosimetry (MIP) were employed as main characterization techniques.

2. Experimental program

A commercial CSA cement, supplied by an Italian cement manufacturer, was used for this study. BFAs samples were collected from the baghouse filter of a thermal power plant burning woodchips located in Basilicata Region (ITALY). Table 1 reports the chemical composition of both materials, evaluated by means of X-ray fluorescence analysis (BRUKER Explorer S4 apparatus); a BRUKER D2 PHASER diffractometer (CuKα radiation and $0.02°2\theta\ s^{-1}$ scanning rate) was utilized for the identification of the main mineralogical phases of BFAs and CSA cement. The Rietveld refinement (carried out through the TOPAS software, Table 1) was employed only for the quantitative mineralogical determination of CSA cement. Due to the high alkali content, (Na_2O and K_2O), BFAs underwent a WWP using a distilled water/BFAs equal to 10. The washing process was carried out by means of a magnetic stirrer at 1500 rpm for 2 hours at room temperature. The chemical composition of "washed BFAs (W_BFAs)" is shown in Table 1 which also reports the specific gravity values (estimated with a pycnometer) and the specific surface (measured according to EN 196-6) of the investigated materials.

Table 1: Chemical, mineralogical composition and physical properties of the binder components

Chemical composition (wt%)				Mineralogical phase composition (wt%)		
	CSA cement	BFAs	W_BFAs	CSA cement	ICDD reference number	
CaO	44.58	40.09	42.20	Ye'elimite	30-0256	43.0
SiO_2	8.95	26.30	27.68	β-belite	33-0302	21.7
Al_2O_3	22.42	6.82	7.18	Celite	38-1429	3.8
Fe_2O_3	1.86	3.04	3.20	Anhydrite	37-1496	19.1
TiO_2	1.10	0.34	0.36	Calcite	05-0586	1.1
K_2O	0.30	7.38	3.62	Brownmillerite	30-0256	4.5
MnO	0.08	0.19	0.19	Gehlenite	73-2041	1.6
Na_2O	0.08	2.08	1.25	Others		5.2
MgO	0.94	3.09	4.20			
Cl^-	0.07	1.02	0.23			
SO_3	16.85	2.07	2.18			
P_2O_5	0.05	3.38	3.40			
l.o.i.*	2.16	4.09	4.30			
Total	99.44	99.89	99.99	Total		100.0
Specific gravity (g/cm^3)	3.11	2.57	2.51			
Specific surface (cm^2/g)	4500±50		4800±50			

*l.o.i.=loss on ignition measured at 950°±10°C

W_BFAs were also submitted to XRD analysis; the EVA software was employed for the evaluation of both patterns and amorphous content of BFAs and W_BFAs. Two CSA blended cements (CSA_10 and CSA_20), respectively containing 10% and 20% by mass of W_BFAs, were investigated; a plain CSA cement (CSA_R) was used as a reference term. For each system, twenty-one mortar prisms were prepared according to the European Standard EN 196-1. After demolding, with the exception of the samples cured for 4 and 24 hours, mortar prisms were placed under water at 20°±1°C until compressive mechanical strength test was carried out

(at 4 and 24 hours and 2, 7, 28 and 56 days). A 0.50 water/solid mass ratio was employed for the preparation of CSA-based cement pastes; they were cast into small plastic vessels and positioned in a thermostatic bath at room temperature for aging periods from 4 hours up to 56 days. At the end of each aging period, every specimen was broken in half: one part was submitted to MIP analysis, the other was finely pulverized (grain size <63μm) for XRD and DT–TG measurements. Both the hardened fragments and powders were primary treated with acetone (to stop hydration) and diethyl ether (to remove water) and then stored in a desiccator containing silica gel and soda lime (to ensure protection against H_2O and CO_2, respectively). Six prisms paste samples (15X15X78 mm) were submitted to dimensional stability test; the prisms were cured in air at room temperature for 4 hours and then demolded. Three samples were aged at 20°C under tap water, the others were stored in a chamber at 50% R.H. and 20°C. Length changes were determined as average values of three measurements taken with a length comparator apparatus.

3. Results and discussion

Ye'elimite was the main phase of CSA cement (43.0 wt%); belite and calcium sulfate, mainly deriving from the addition of natural anhydrite, were present as secondary components. BFAs were "high-calcium biomass fly-ashes" owing to their high content in CaO (40.09 wt%) with regard to SiO_2 amount (26.30 wt%); the ashes were also rich in K_2O (7.38 wt%) and low in (I) Na_2O (2.08 wt%), (II) SO_3 (2.07 wt%) and (III) Cl (1.02 wt%). After the WWP, W_BFAs were much lower in alkalies (Na_2O_{eq}=3.64 wt%). XRD analysis revealed that quartz, mullite, hematite and CaO_f (free CaO) were the main crystalline phases for both BFAs and W_BFAs; additionally, their amorphous content was equal to 45 wt% and 48 wt%, respectively. The time development of mechanical compressive strength of the three systems is reported in Figure 1.

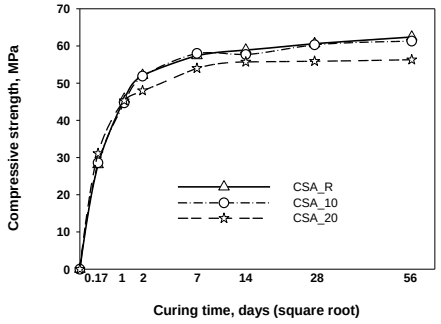

Figure 1: Compressive strength values for CSA_R, CSA_10 and CSA_20 cured at various periods.

For all the investigated curing periods, it was found that: a) the compressive strength for CSA_R and CSA_10 based-mortars were almost similar to each other; b) CSA_20 based-mortar, compared with the afore mentioned systems, exhibited compressive strength values higher after 4 hours of hydration, almost equal after 1 day and about 8% lower at curing periods longer than 14 days.
Figure 2 shows the length change *vs.* curing time for the three systems; they differed very little from each other, both when submerged under water and cured in air.

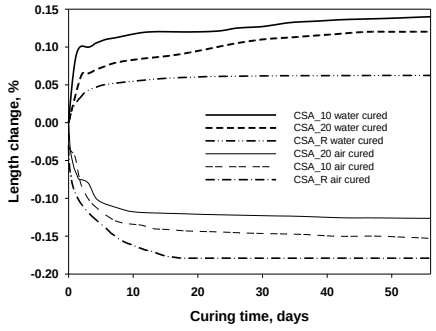

Figure 2: Dimensional stability curves for CSA-based cements (air and water cured).

The maximum expansion values, comprised in the narrow range 0.06-0.19%, were reached after about 14 days of curing for the samples cured under water; on the contrary, the pastes cured in air exhibited a continuous shrinkage until 14 days when a minimum length change was reached (-0.17%, -0.15% and -0.13% for CSA_R, CSA_10 and CSA_20, respectively). Figure 3 displays the DT results for CSA_R, CSA_10 and CSA_20

hydrated for different curing times (4 and 24 hours, 7, 28 and 56 days). With DT–TG temperature increase, three different endothermal effects were identified (at 109°±4°C, 166°±4°C and 285°±2°C) and attributed, in the order, to the following hydration products (Taylor,1997): $CaO{\cdot}SiO_2{\cdot}H_2O$, $3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$ and $Al_2O_3{\cdot}3H_2O$; furthermore, except for the peak related to $CaCO_3$ present in W_BFAs, no significant effects were found above 500°C.

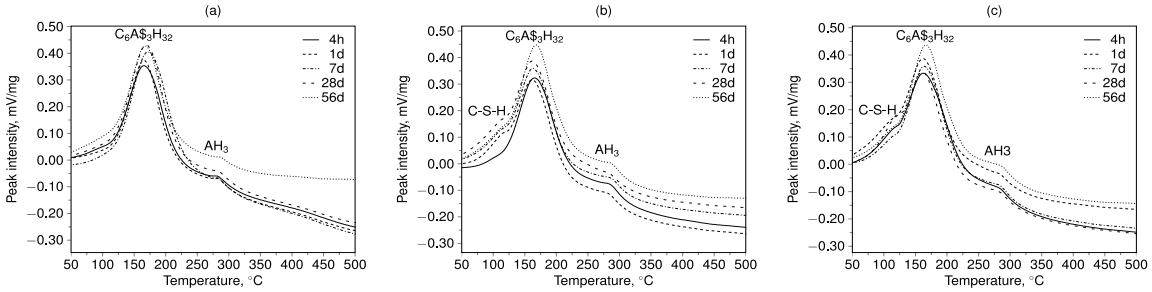

Figure 3: DT results for CSA_R (a), CSA_10 (b) and CSA_20 (c) hydrated for 4 hours, 1, 7, 28 and 56 days. Legend: $CaO{\cdot}SiO_2{\cdot}H_2O$=C-S-H; $3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$=$C_6A\$_3H_{32}$; AH_3=$Al_2O_3{\cdot}3H_2O$.

On the whole, the DT results revealed the presence of $3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$ and $Al_2O_3{\cdot}3H_2O$ for all the curing periods while $CaO{\cdot}SiO_2{\cdot}H_2O$ was detected only in the systems containing W_BFAs thanks to the hydration of their reactive CaO and SiO_2; furthermore, both $3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$ and $Al_2O_3{\cdot}3H_2O$ concentrations increased with aging time. In general, these outcomes suggested that: I) the hydration behavior of CSA_R are chiefly regulated by the reaction of ye'elimite with calcium sulfate; II) the hydraulic performances of both CSA_10 and CSA_20 also depend on the self-cementing properties of W_BFA reactive components. The hydration evolution for the three systems was also evaluated in terms of chemically bound water (Figure 4) calculated on the basis of the mass loss values (up to 500°C) from TG analyses.

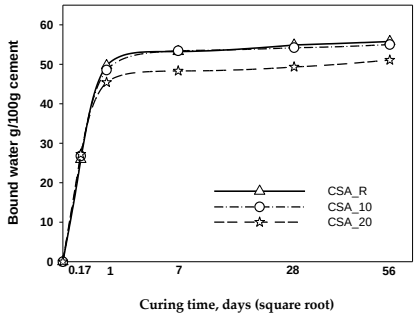

Figure 4. Bound water as determined up to 56 days of hydration (normalized to 100g of anhydrous cement) for CSA_R, CSA_10 and CSA_20 plotted against curing time.

Figure 4 indicates that the three systems followed a similar trend in terms of hydration process evolution; additionally, except for CSA_20, the other binders reached comparable bound water values at 56 days of curing. XRD outcomes confirmed the indications given by DT-TG analyses. From these results it can be ascertained that the hydraulic activity of W_BFAs does not influence the mechanical properties of CSA_10, while only a low decrease of the compressive strength is shown when 20% of biomass ash was added to CSA cement; these findings are confirmed by MIP investigations.

Figure 5 displays the porosimetric curves for hydrated cement pastes of the investigated systems; the top and the bottom part of the Figure respectively reports the cumulative and derivative plots for intruded Hg volume of CSA-based cements *vs.* pore radius at various curing times (from 4 hours to 56 days). A unimodal pore size distribution, centred on the lowest width of pore necks connecting a continuous system, is observed for CSA_R (Figure 5 (a)) at all the curing periods [6]; in particular, with the increase of curing time, both cumulative pore volume and threshold pore width respectively decrease from 225 to 120 mm^3/g and from about 210 to 20 nm. In comparison to CSA_R, the other two systems show a different behaviour: a multimodal pore size distribution, already present after 4 hours of hydration, is found at all the investigated curing times; moreover, for CSA_10, due to high reaction rate, the cumulative pore volume reduces of about 37% (from 258 to 162 mm_3/g) from 4 hours to 2 days; on the contrary, at longer curing times, this value is almost constant (~108 mm^3/g). At the earliest and longest curing times, the first and the last thresholds pore widths respectively shift from 400 to 118 nm and from 5 to less than 3.6 nm. Similar porosimetric features are also observed for CSA_20 system.

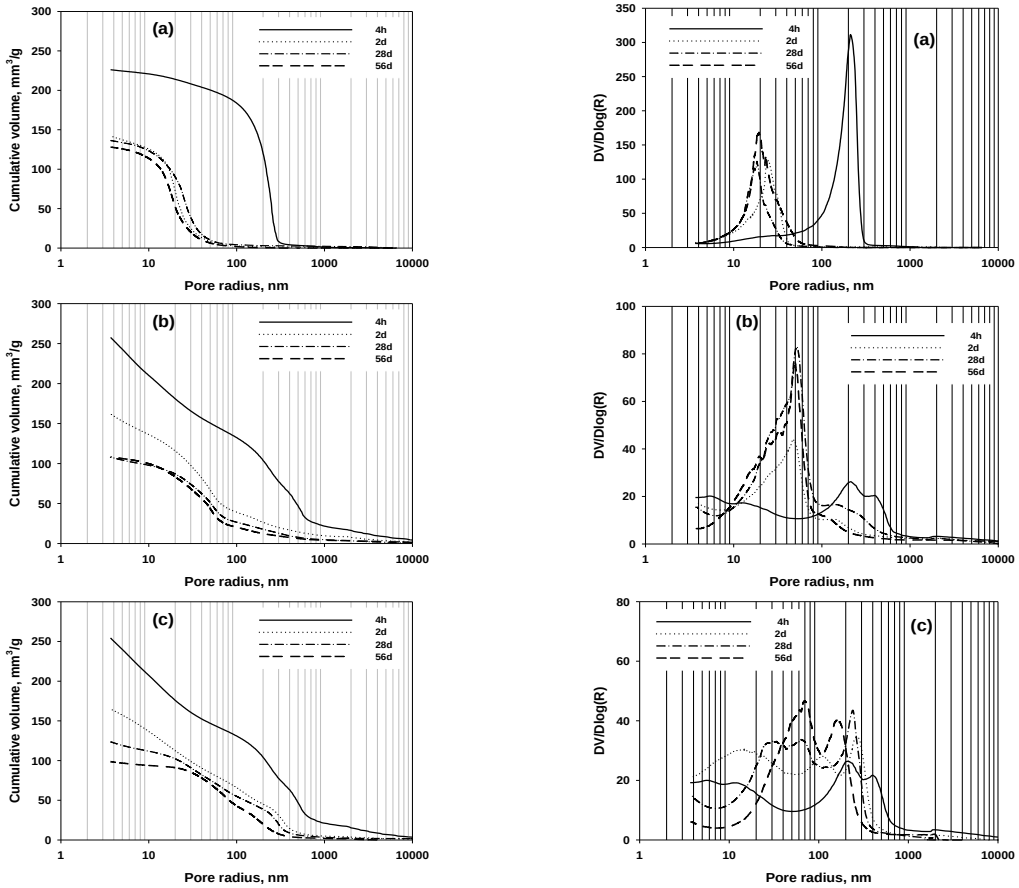

Figure 5: Cumulative (left) and derivative (right) Hg volume vs. pore radius for CSA_R (a), CSA_10 (b) and CSA_20 (c) pastes cured from 4 hours to 56 days.

4. Conclusions

In this paper the possibility of using biomass fly ashes (BFAs), as alternative supplementary cementitious materials (SCMs) in calcium sulfoaluminate (CSA)-blended cements, was evaluated. BFAs were first submitted to a water washing process (W_BFAs) with the aim of reducing the high alkali content. W_BFAs are very interesting since their utilization as SCMs, in addition to the saving of raw materials and waste landfilling, allows the CSA cement dilution which implies both a decreased emission of CO_2 and a noticeable energy saving per unit mass of manufactured cement. W_BFAs were mainly composed by reactive calcium-, silicon- and aluminum-oxides which react with water to give calcium silicate hydrate responsible for its binder properties. On the whole, the experimental results demonstrated that the use of W_BFAs (up to 20% by mass) in CSA-blended cements did not appreciably influence mortars compressive mechanical strength, pastes dimensional stability and hydration behaviour.

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