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Use of alkaline salts to improve the reactivity of cements with high fly ash content: hybrid alkaline cements

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ABSTRACT

It is known that the activities carried out throughout the production cycle of Portland cement result in serious environmental impacts. This negative circumstance must be counteracted by introducing into the cement industry and the building and construction sector more sustainable practices that could meet the principles of circular economy and the targets of the Sustainable Development Goals included in the United Nations 2030 Agenda for Sustainable Development. A possible solution within this context is to foster the use of hybrid cements, a combination of Portland cement with alkaline cements, in which a significant amount of supplementary cementitious materials is used for replacing the former. The effect of adding a mixture of alkaline salts (Na_2SO_4 + NaCl) to improve the development of early-age mechanical strengths in cements having high contents of fly ash (45% and 65%) in place of Portland cement was analysed in this work. The mechanical strength values of those cement pastes were determined for curing ages of 2, 28, 90 and 180 days and compared to the behaviour of an ordinary Portland Cement CEM I 42,5R. The rate of heat release and total heat were determined by isothermal conduction calorimetry. The reaction products were characterized by X-ray diffraction and scanning electron microscopy. The results of the mechanical strength tests indicated that the hybrid alkaline cement having 45% of fly ash showed a similar behaviour to the reference cement for a curing age of 28 days, which is an interesting achievement. The findings of the investigation allow considering the possibility of using these types of cements in non-strucutural concrete products within the context of the precast concrete industry. Such solution will be an important green deal between the cement industry and the environment and will aid the introduction of circular and sustainable practices within the building and construction sector.

KEYWORDS: *Hybrid alkaline cements, fly ash, alkaline salts, mechanical strength, microstructural characterization.*

1. Introduction

Worldwide efforts are being carried out to introduce into the different economic sectors circular and sustainable practices that could provide a more pleasant quality of life to society. The United Nations 2030 Agenda for Sustainable Development, which includes the 17 Sustainable Development Goals (UN, 2022), is serving as a compass to achieve such outcome.

The building and construction sector is responsible for generating serious environmental impacts caused by the large-scale consumption of natural resources and energy. To counteract this scenario, it is important to foster the use of alternative binders to ordinary Portland cement. Hybrid alkaline cements

might be a step towards that goal. These cements are composed by a combination of Portland clinker with a significant amount of supplementary cementitious materials (SCMs), as a source of aluminosilicate compounds, such as fly ash, and an alkaline activator (Qu *et al.*, 2016; Sanchéz-Herrero *et al.*, 2019).
The main goal of this work was the study of hybrid alkaline cements using fly ash as SCM and a mixture of two alkaline salts (Na_2SO_4 + NaCl) to perform the role of activator. Two hybrid alkaline cements were investigated by carrying out mechanical strength tests, isothermal conduction calorimetry, X-ray diffraction (XRD) and blackscattered scanning electron microscopy (BSEM)/energy dispersive X-ray (EDX). An ordinary Portland cement hydrated with water was also prepared for comparison purposes.

2. Experimental

Ordinary Portland cement CEM I 42,5R (OPC), fly ash (FA) provided by a Portuguese coal power plant and a combination of the alkaline salts Na_2SO_4 and NaCl from Panreac, which were provided in the anhydrous form, were used to prepare the cements. The chemical composition of OPC and FA, determined by X-ray fluorescence using a BRUKER S8 Tiger spectrometer, can be consulted in Table 1. FA was ground in a ball mill, leading to a circumstance in which around 99% of its particles were below 32 µm (the particle size distribution was evaluated using laser diffraction technique on a Coulter LS 130). In the case of the original FA, only about 65% of the particles were below that dimension.

Table 1. Chemical composition of OPC and FA.

Material	Compound (weight %)											
	Al_2O_3	SiO_2	CaO	Na_2O	Fe_2O_3	SO_3	Cr_2O_3	MgO	TiO_2	K_2O	Other	LOI[a]
OPC	4.64	18.40	61.60	0.28	3.27	3.23	0.01	1.32	0.47	0.97	5.81	4.00
FA	21.44	56.11	1.30	1.12	8.20	0.66	5.05	1.46	1.15	2.81	0.70	5.05

[a]Loss on ignition

Hybrid alkaline cements including the precursors OPC and FA and a combination of Na_2SO_4 and NaCl in solid form were prepared in accordance with Table 2. For comparison purposes, it was also manufactured a reference cement including exclusively OPC. After mixed with water, the pastes were casted into prismatic moulds 1 × 1 × 6 cm. The workability of the cements was evaluated by conducting mini-slump tests according to Kantro (1980). Results have showed quite similar behaviours: consistencies of 76, 74 and 67 mm were found to BOPCR, BOPC50 and BOPC30, respectively.

Table 2. Composition of the cement pastes.

Paste	Raw material (weight %)				w/b[a]
	OPC	FA	Na_2SO_4	NaCl	
BOPCR	100	—	—	—	0.28
BOPC50	50	45	2.5	2.5	0.28
BOPC30	30	65	2.5	2.5	0.28

[a]w/b = water/binder ratio (binder corresponds to the sum of OPC, FA and activator)

Five samples of each cement were submitted to compressive strength tests on a IBERTEST AUTOTEST 200/10 SW under displacement control at a rate of 0.07 $kN \cdot s^{-1}$ for 2, 28, 90 and 180 days (the results, which show the standard deviation, are presented without outliers). After each curing age, samples were ground and forwarded to characterization by XRD on a BRUKER D8 ADVANCE diffractometer under CuKα radiation (40kV y 30 mA). The rate of heat release and total heat of the cements were monitored on a conduction isothermal calorimeter from TAM AIR working at a temperature of 25ºC. In addition, the reaction products were submitted to BSEM analysis on a Hitachi S-4800 scanning electron microscope (20 kV) prepared with an Oxford LINK-ISIS X-ray energy dispersive analyser.

3. Results and discussion

The results of the compressive strengths displayed in Figure 1 show that there were meaningful losses of resistance for the cements in which OPC was replaced by FA at early-age curing ages. The presence of the alkaline salt prevented the losses from being even higher. However, the increase of the curing time tended to neutralize those differences, especially in the case of BOPC50, which showed a similar behaviour to the reference cement from 28 days onwards (compressive strengths above 60 and 40 MPa were found after 28 days for, respectively BOPC50 and BOPC30).

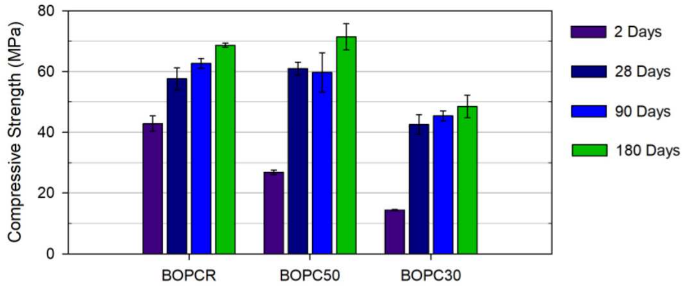
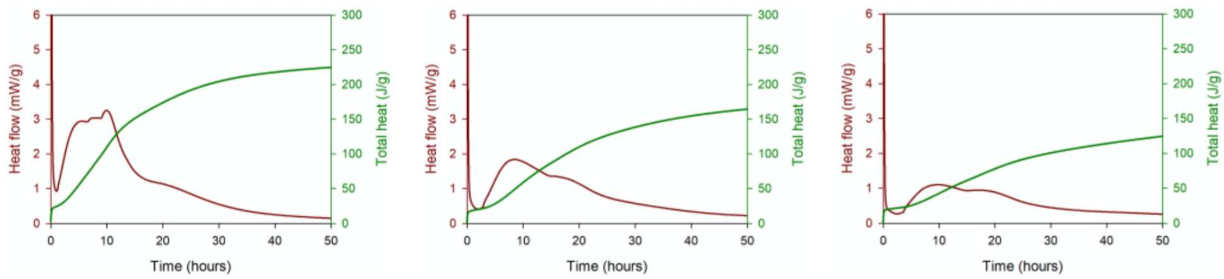


Figure 1. Compressive strength of the cements.

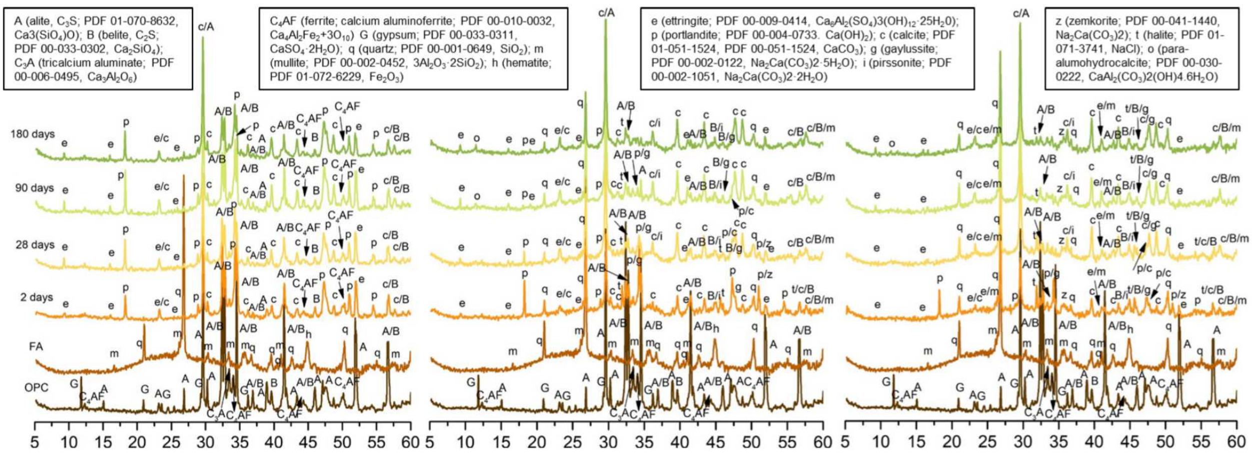
The heat flow and total heat released by the cements provided in Figure 2 show similar calorimetric responses for all cements: a first very intense peak, very difficult to detect, followed by a short induction period and then a second peak, much broader than the first one. The second peak is associated with the precipitation of the C-S-H gel, while the shoulder of that peak is related to the reaction of aluminates with sulfates to form AFt or AFm phases (sulfate depletion) (Scrivener *et al.*, 2015). The presence of FA instead of OPC resulted in a lower total heat release by BOPC50 and BOPC30 compared to BOPC.



(a) (b) (c)

Figure 2. Heat flow and total heat released by (a) BOPCR, (b) BOPC50 and (c) BOPC30.

The XRD patterns of the cements and also the anhydrous OPC and FA is exhibited in Figure 3. It was noticed that the signals referring to the crystalline phases of FA the did not disappear overtime. The peaks associated with clinker phases (alite, belite, tricalcium aluminate and ferrite) tended to disappear with the curing time, or their intensity decreased.



(a) (b) (c)

Figure 3. XRD patterns for (a) BOPCR, (b) BOPC50 and (c) BOPC30.

The intensity of portlandite-related peaks is lower in BOPC50 and BOPC30, which could be explained by: 1) lower cement content, lower portlandite generation; 2) portlandite consumption by the reaction between this phase and the alkaline salt, to generate *in situ* alkalinity; 3) the reaction with FA at highest curing ages (pozzolanic reaction) or 4) carbonation: the intensity of the peaks associated with calcite tended to increase with curing time for hybrid cements. For these cements, the presence of other carbonates such as gaylussite, pirssonite or zemkorite was also observed.
The BSEM/EDX analysis performed for BOPC30 at 28 days, and that is displayed in Figure 4, shows the coexistence of a mixture of cementitious gels C-A-S-H/(N,C)-A-S-H, which is the main reaction product of these types of hybrid cements. The composition of the gels included in the matrix were influenced by the presence of OPC/FA particles. Close to OPC particles, the gel had high contents of Ca and Si and a minor amount of Al. On the other hand, high contents of Si and Al and smaller amounts of Ca were noticed around FA particles. A common element of these gels is Na, which was provided by the alkaline salts used as activator.

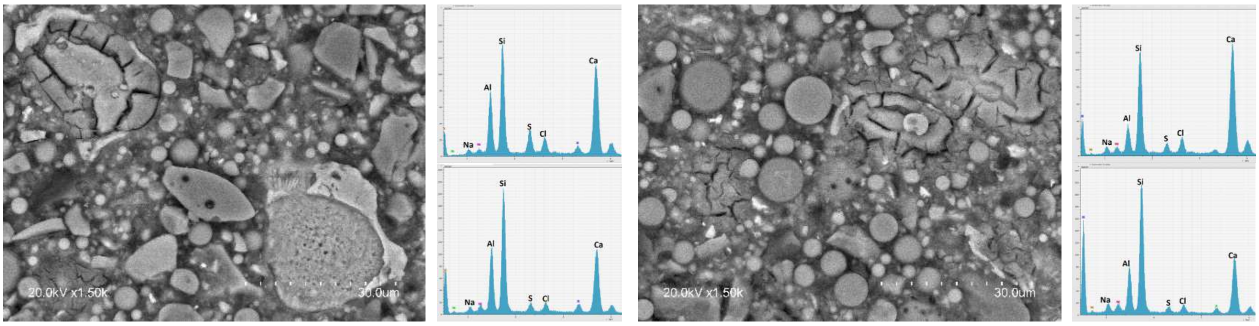


Figure 4. BSEM micrographs and EDX analyses for BOPC30 after 28 days of curing.

4. Conclusions

Cements including residues as raw materials should be studied in order to develop sustainable alternatives to OPC. The hybrid alkaline cements using fly ash in large amounts as SCM and a mixture of Na_2SO_4 + NaCl as activator investigated in this work showed potential to play that role. It should be highlighted the quite interesting mechanical behaviour of these cements from 28 days onwards. The reason for this outcome is the coexistence in the matrix of the main reaction product of these cements, which were the cementitious gels C-A-S-H/(N,C)-A-S-H. These results might act as a lever to promote the use of these cements in the manufacture of non-structural concrete products (without reinforcement).

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