



# Variation in hybrid cements over time. Alkaline activation of fly ash–portland cement blends



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## ABSTRACT

The primary aim of the present paper was to determine the variations over time (one year) in the main cementitious gels forming during the alkaline activation of hybrid cements (70% FA/30% OPC). The 28 and 365 day hydration products were characterised by different techniques. The findings showed that the C-S-H/N-A-S-H mix of gels precipitating did not precipitate in a pure state, but rather that their composition was affected by the presence of dissolved species. In the presence of aluminium C-S-H gel development was: C-S-H → C-(A)-S-H → C-A-S-H, whilst in the presence of calcium, N-A-S-H gel evolved as follows: N-A-S-H → (N,C)-A-S-H → C-A-S-H. This last conversion is not complete in these systems because the amount of calcium present is thought to be insufficient. On the grounds of the findings, a microstructural model is proposed to describe the development of the reaction products forming in these hybrid cements.

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## 1. Introduction

Concerns around the CO<sub>2</sub> emitted during portland cement manufacture have driven the scientific community to seek alternative materials with the same features as portland cement but which can be sustainably manufactured.

Portland cement has been effectively replaced by SCMs (supplementary cementitious materials such as slag, natural pozzolans or ash) for many years, as amply documented in the literature [1–8]. This practice has, moreover, been acknowledged by legislation the world over as a way of generating different types of cement. All authors have generally

reported that the use of SCMs leads to significant improvements in cementitious systems whilst contributing to sustainability.

The use of fly ash as a partial replacement for portland cement, in addition to effectively reducing cement consumption, provides a solution for recycling this industrial by-product. A considerable number of references can be found in the literature on water-hydrated OPC–FA systems in which OPC replacement by FA varies over a wide range [9–12]. European standard EN 197 limits the replacement ratio to under 35% for type II cements and under 55% for type IV cements [13], primarily because at higher percentages the early age mechanical strength of the cement declines substantially (when used alone, fly ash exhibits no hydraulic behaviour).

One proposal (and one of the principal aims of the present study) for raising the ash content in OPC blends to 70% without compromising

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initial mechanical strength development is the alkaline activation of the materials at ambient temperature.

The alkali activation of fly ashes (aluminosilicates) is a line of research that is obtaining very promising results in terms of the properties of the cements produced [14,15]. The main differences between this procedure and normal portland cement hydration are the high alkaline content and the substantially lower total calcium content in the materials. In these systems the reaction product to which mechanical strength development and durability are attributed is a N-A-S-H gel, a three-dimensional alkaline aluminosilicate structure [14–16] very different from the C-S-H gel, the calcium silicate hydrate obtained in OPC hydration [17].

The reaction products forming during the alkaline activation of cement and ash blends is an area of keen scientific and technological interest, and the compatibility between the two cementitious gels, N-A-S-H and C-S-H (the main hydration products in the OPC–fly ash–alkali system), is the object of considerable research today [18–20]. Earlier studies have shown that the co-precipitation of these two gels in hybrid cements is possible [21–26], although recent research has revealed that the two products do not develop separately as two distinct gels, but that they interact, undergoing structural and compositional changes in the process [20].

Recent studies on synthetic samples to analyse C-S-H/N-A-S-H compatibility in greater depth showed that the stability of the N-A-S-H structure in the presence of calcium depends heavily on the pH in the medium [20]. In the presence of sufficient calcium, pH values of over 12 favour the formation of a C-A-S-H rather than a N-A-S-H gel [19,20]. The experiments yielding these findings were conducted in equilibrium conditions, however, which are not normally in place during binder hydration, particularly in the early stages of the reaction. The scientific evidence would appear to show that whilst reaction kinetics stimulates the early age formation of both types of gels, over time a C-A-S-H type gel would be the most thermodynamically stable product. Nonetheless, since the co-precipitation of the two gels (C-S-H + N-A-S-H) has been described for short reaction times (28 days at most) only [21–23], no information on the variations in these blends at longer reaction times (such as 1 year) has been forthcoming. In light of that knowledge gap, the present study aimed to determine the variations over time in the main cementitious gels formed in non-equilibrium conditions during the alkaline activation of hybrid cements consisting of 70% FA and 30% OPC.

## 2. Experimental

### 2.1. Materials

The prime materials used in this study were commercial 52.5 NSR portland cement, supplied by MOLINS SA (Spain), and a type F fly ash (ASTM C618-94) [27] from the coal-fired steam plant at Puentenuovo, likewise in Spain. The chemical composition of the materials given in Table 1 was determined as specified in the European standard EN 196-2 [28] for the cement and as recommended in the Spanish standard UNE 80-225-93 [29] for the fly ash (wet chemistry method).

The hydration liquids used were deionised water (hereafter W) and an alkaline solution containing 12.5-M NaOH and sodium silicate (both included in the liquid phase), with a SiO<sub>2</sub>/Na<sub>2</sub>O ratio of 0.66 and a density of 1.2 g/cm<sup>3</sup> (hereafter A). The soluble silica in the alkaline solution was essentially in the form of Q<sup>0</sup> units (monomers), guaranteeing high reactivity [30]. The choice of the activator used (12.5-M NaOH + Na<sub>2</sub>SiO<sub>3</sub> mix) was based on prior studies in which the inclusion of soluble silica in the medium was observed to improve the development of mechanical strength in the material [31].

### 2.2. Methodology

The paste specimens were made with 70:30 (wt) blends of fly ash and portland cement (M: 70% FA + 30% OPC wt.), (liquid/solid ratio,

**Table 1**  
Chemical composition of the materials (wt.%).

	SiO <sub>2</sub>	CaO	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	SO <sub>3</sub>	Na <sub>2</sub> O <sup>4</sup> <sub>eq</sub>	Other	LOI <sup>5</sup>	IR <sup>6</sup>
OPC <sup>1</sup>	20.26	62.79	6.33	2.30	0.18	2.82	0.75	–	2.56	0.73
FA <sup>2</sup>	54.32	3.11	25.22	7.01	1.69	0.01	2.47	3.46	2.09	0.66
M <sup>3</sup>	44.09	21.07	19.55	5.59	1.23	0.853	1.949	5.66	2.231	0.681

(1) Portland cement; (2) fly ash; (3) M: 70% FA + 30% OPC; (4) Na<sub>2</sub>O<sub>eq</sub>: Na<sub>2</sub>O wt.% + 0.658 K<sub>2</sub>O wt.%; (5) loss on ignition; (6) insoluble residue.

0.35). The main characteristics of the systems studied are given in Table 2.

These pastes were moulded into specimens measuring 1 × 1 × 6 cm and cured for 24 h in a chamber at 21 °C and 99% relative humidity. The specimens were then removed from the moulds and stored in the chamber until the test age.

The 28- and 365-day compressive strength of the specimens was determined on an Ibertest (Autotest-200/10-SW) test frame (12 replicates per matrix and per age). After testing, the pastes were ground, immersed in acetone, washed with ethanol and dried in a desiccator prior to further analysis. The matrices were characterised mineralogically and microstructurally with XRD, BSEM/EDX, TEM/EDX and <sup>29</sup>Si, <sup>27</sup>Al and <sup>23</sup>Na MAS NMR.

X-ray diffractograms of powdered samples were obtained with a Phillips PW 1730 CuKα diffractometer (40 kV, 50 mA). Specimens were step-scanned at 2° min<sup>-1</sup>, with a 2θ angle of 2–60°, a 1° divergence slit, a 1° anti-scatter slit and a 0.1-mm receiving slit. In BSEM analysis, polished sections of the samples were carbon coated and studied under a JEOL JSM 5400 scanning electron microscope (20.0 kV) fitted with a solid-state BSE detector and a LINK-ISIS energy dispersive X-ray (EDX) analyser. TEM characterisation was conducted using a JEOL JEM 2000 FX (200 kV, resolution 0.31 nm). TEM microscope fitted with a LINK ISIS EDX analyser (The analyses were conducted on powder samples dispersed in isopropanol over a copper grid).

Lastly, the gels were analysed with a Bruker Avance-400 MAS NMR spectrometer under the following conditions: <sup>29</sup>Si resonance frequency, 79.5 MHz; spinning rate 10 kHz; pulse sequence, single pulse (5 μs); recycle delay, 10 s; number of transients, 4912; external standard, TMS (tetramethylsilane); <sup>27</sup>Al resonance frequency, 104.3 MHz; spinning rate, 10 kHz; recycle delay, 5 s; pulse sequence, single pulse (2 μs); number of transients, 400; external standard, Al(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup>; <sup>23</sup>Na resonance frequency, 105.8 MHz; spinning rate, 10 kHz; recycle delay: 5 s; pulse sequence, single pulse (2 μs); number of transients, 160; and external standard, NaCl.

## 3. Results

### 3.1. Mechanical strength

Fig. 1 shows the variations in compressive strength over time in the water-hydrated (MW) and the alkali-activated (MA) blends. As expected, mechanical strength rose with time in both systems.

Both the 28- and 365-day pastes hydrated in the presence of the alkaline activator had higher mechanical strength than observed in the respective water-hydrated pastes. As discussed below, this finding suggests that all the traditional products formed during water hydration of these mixes differ from the products obtained during alkali activation.

**Table 2**  
Batching of matrices studied.

	FA content (g)	OPC content (g)	Hydration liquid	L/S ratio
MW	70	30	Water (W)	0.35
MA	70	30	NaOH 12.5 M + Na <sub>2</sub> SiO <sub>3</sub> (A)	0.35

W: water; A: NaOH 12.5 M + Na<sub>2</sub>SiO<sub>3</sub> (ρ = 1.2 g/cm<sup>3</sup>).

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