Low environmental impact hybrid cements: reducing clinker content

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ABSTRACT

The environmental problems posed by portland cement manufacture have prompted the scientific committee to seek more eco-efficient binders with the same technological features as OPC; hybrid cements are among such alternative materials. Hybrid alkaline cements are multi-component systems containing a high mineral addition (fly ash (FA), metakaolin (MK), blast furnace slag (BFS)) content, low proportions (<30 %) of portland clinker and moderately alkaline activators. The substantially lower amount of clinker needed to manufacture these binders than ordinary portland cement is both economically and ecologically beneficial. The present study explored strength development and the reaction products generated by several hybrid cements, consisting of a number of industrial by-products and very low portland clinker contents.
Keywords: alkaline activation; geopolymer; hybrid cements; mechanical strength; NMR.

RESUMEN

La problemática medioambiental en torno a la fabricación de cemento portland, ha llevado a la comunidad científica a buscar nuevos materiales cementantes alternativos, mas ecoeficientes, y con las mismas prestaciones tecnológicas que las del cemento portland tradicional, en este sentido se ha desarrollado los cementos híbridos. Los cementos híbridos alcalinos son interesantes sistemas multicomponente que incorporan elevados contenidos de adiciones minerales (cenizas (FA), metacaolin (MK), escorias (BFS)…) y bajos contenidos de clinker portland (CK) (< 30 %), junto con activadores de moderada alcalinidad. El desarrollo de estos cementos permite una importante reducción en el factor clinker, con el beneficio tanto económico como medioambiental que ello supone. En el presente trabajo se investiga tanto el desarrollo resistente como los productos de reacción generados en diferentes cementos híbridos, constituidos por diversos subproductos industriales y muy bajos contenidos en clinker portland.
Palabras clave: activación alcalina; geopolimero; cementos híbridos; resistencia mecánica; RMN.

RESUMO

A questão ambiental em torno da fabricação do cimento Portland levou a comunidade cientifica a buscar por novos materiais cimentícios alternativos, porém ecoeficientes e com prestações tecnológicas semelhantes às do cimento Portland tradicional. Uma alternativa, nesse sentido se desenvolveram os cimentos híbridos. Os cimentos híbridos alcalinos são interessantes sistemas multicomponentes que incorporam elevados conteúdos de adições minerais (cinzas (FA), metacaulim (MK), escórias (BFS)...) e baixos conteúdos de clínquer Portland (CK) (<30%), junto com ativadores de moderada alcalinidade. O desenvolvimento destes cimentos permite uma importante redução do fator clínquer, com benefício econômico e também ambiental. Neste presente trabalho é investigado tanto o desenvolvimento da resistência como os produtos das reações gerados dos cimentos híbridos, constituídos por diferentes produtos industriais e conteúdos baixos de clínquer Portland.
Palavras-chave: Ativação alcalina; geopolimero; cimento hibrido; resistência mecânica; RMN.

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1. INTRODUCTION

Portland cement is the material most widely used in construction today. Its mass production raises substantial energy and environmental issues, however. It calls for large amounts of energy to heat the raw materials to temperatures of up to 1400-1500 ℃, while the extraction of raw materials depletes natural quarries and scars the landscape, and the manufacturing process entails the emission of greenhouse gases such as -CO_2 and NO_x. With 0.8 tonnes of CO_2 per tonne of cement manufactured, the industry accounts for 7-8 % of worldwide emissions of this greenhouse gas (Gartner, 2001).

One of the approaches, widely accepted today, to reducing this impact while helping solve other environmental problems (finding a use for industrial by-products or waste that would otherwise be the object of costly and pollution-prone stockpiling) is to include active industrial by-product or mineral additions in portland cement clinker. This gives rise to different types of ordinary cements, officially recognised in Spanish and European standard UNE-EN 197-1:2000, which specifies both the type and maximum amount of additions allowed. Another more innovative option consists of developing alternative, less expensive and where possible less environmentally damaging cements (involving lower CO_2 emissions or the re-use of industrial by-products) whose characteristics or performance are comparable to or even better than ordinary Portland cement (OPC). Such binders are generically known as "*alkaline cements*" (Palomo et al., 1999; Shi et al., 2006,; Provis and Deventer, 2009).

Alkaline cements are a type of binders formed as the result of dissolving industrial waste or natural aluminosiliceous materials (with amorphous or vitreous structures) in an alkaline medium. When mixed with alkaline activators these materials set and harden, yielding a material with good binding properties. The two major alkaline activation models in place can be distinguished by their starting conditions.

-*Model 1:* activation of *high calcium and high silicon* materials (Me_2O-MeO-Al_2O_3-SiO_2-H_2O system)**;** an example of this first model is the activation of blast furnace slag (SiO_2+CaO > 70 %) under relatively moderate alkaline conditions. The main reaction product is a *C-S-H* (calcium silicate hydrate) gel similar to the gel obtained during portland cement hydration, although with a small percentage of Al in its structure (C-(A)-S-H gel) (Fernández-Jiménez et al., 2003).

-*Model 2:* activation of materials comprising primarily aluminium and silicon (Me_2O-Al_2O_3-SiO_2-H_2O system). The materials used in this second alkaline activation procedure, such as metakaolin or type F fly ash from coal-fired steam power plants, have low CaO contents. Here more aggressive conditions (high alkalinity and curing temperatures of 60 to 150 ℃) are required. The main reaction product formed is a three-dimensional alkaline inorganic polymer, a *N-A-S-H* (alkaline silicoaluminate hydrate) gel that may be regarded as a *zeolite precursor* (Palomo et al., 2004; Fernández-Jiménez et al., 2006; Duxon et al., 2007).

A third model based on a combination of the above two has recently appeared, however. The latest research has shown that the presence of a certain amount of reactive calcium (in the form of portland clinker) in the starting mix enables the material to harden at ambient temperature with no need for initial thermal activation. These alkali-activated cements with less than 30 % portland cement clinker are known as "*hybrid cements*" (Palomo et al., 2007). In light of the enormous versatility respecting the raw materials that can be used (large proportions of industrial by-products such as fly ash, slag or metakaolin), considerable scientific and technological attention has been focused on hybrid cements.

According to some authors, the reaction product is a mix of the two gels (C-S-H + N-A-S-H) (Palomo et al., 2007; García-Lodeiro et al., 2010a, 2010b and 2011), while others maintain that it is an entirely different substance (Yip et al., 2005).

The present study attests to the enormous versatility of low (20 %) clinker, multi-component hybrid cement systems and the good mechanical performance of the respective binders. It also addresses the mineralogical and microstructural characteristics of these hybrid cements when hydrated in the presence of solid alkalis to induce activation in technologically viable times.

2. EXPERIMENTAL

The raw materials used included commercial clinker (CK), granulated blast furnace slag (BFS), metakaolin (MK) (both from Algeria) and a Slovakian type F fly ash. The metakaolin was obtained by burning the raw material at 750 ºC for 2 hours. The chemical composition of the materials given in Table 1 was determined by XRF on a PHILIPS PW-1004 X-ray spectrometer. Their (XRD-determined) mineralogy is shown in Figure 1.

Table 1. Chemical composition of the materials (XRF, wt% of oxides)

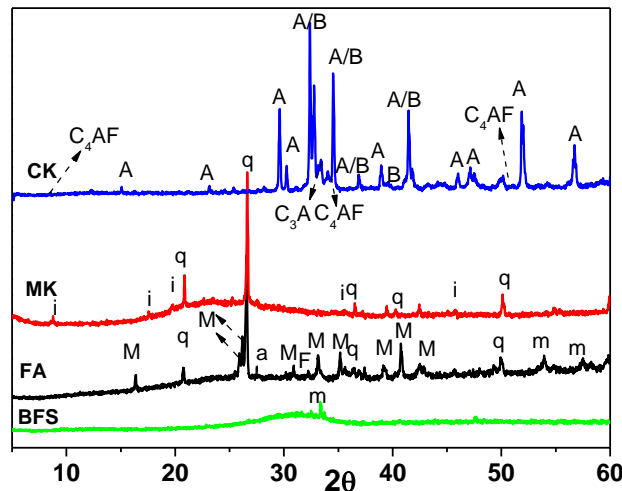|	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	Na_2O	SO_3	K_2O	TiO_2	P_2O_5	LoI[*]
Clinker (CK)	21.83	4.85	61.19	3.20	2.03	0.69	1.11	1.76	0.15	0.48	2.65
Fly ash (FA)	56.51	21.42	3.78	8.57	2.19	0.63	0.99	2.59	0.87	0.15	2.21
Slag (BFS)	36.63	7.25	38.09	0.46	8.51	0.53	2.13	0.62	0.27	0.06	4.88
Metacaolin (MK)	55.03	37.69	0.04	2.89	0.44	0.02	0.02	3.20	0.26	0.24	--

* Loss on ignition at 1 000 ℃ for 1 hour

Figure 1. XRD patterns for the raw materials used: slag (BFS), fly ash (FA), metakaolin (MK), clinker (CK) [symbols: q=quartz *(SiO₂); a = anorthite; M=mullite* $(3Al_2O_3.2SiO_2)$*); F=hematite (Fe₂O₃); m=merwinite (Ca₃Mg(SiO₄); A = alite (C₃S); B=belite (C₂S); C₃A = tricalcium aluminate; C₄AF=ferrite phase*]

Several binders (B) were prepared (see Table 2): binary (B2), consisting of blends of 20 % clinker and 80 % fly ash or slag, and ternary (B3), comprising fly ash (FA) + slag (BFS) + clinker (CK) (with variable percentages of additions and 20 % clinker) or metakaolin (MK) + slag (BFS) + clinker (CK).

Table 2. Binary and ternary binders studied

	FA	BFS	MK	CK	Activator*	w/c**	Label
Binary (B2)	80	--	--	20	**--**	0.40	**B2-FA-H**
	80	--	--	20	A	0.38	**B2-FA-A**
	80	--	--	20	B	0.38	**B2-FA-B**
	--	80	--	20	--	0.26	**B2-BFS-H**
	--	80	--	20	A	0.26	**B2-BFS-A**
	--	80	--	20	B	0.26	**B2-BFS-B**
Ternary (B3)	70	10	--	20	--	0.35	**B3-FA7 -H**
	70	10	--	20	A	0.35	**B3-FA7 -A**
	70	10	--	20	B	0.36	**B3-FA7-B**
	60	20	--	20	--	0.36	**B3-FA6-H**
	60	20	--	20	A	0.35	**B3-FA6-A**
	60	20	--	20	B	0.35	**B3-FA6-B**
	50	30	--	20	A	0.35	**B3-FA5-A**
	50	30	--	20	B	0.35	**B3-FA5-B**
	--	40	40	20	A	0.5	**B3-MK4-A**

As all the blends contained 4 %, the end product contained 96 % binary/ternary binder and 4 % activator
*** water/cement ratio*

The pastes obtained by hydrating the binders with water were moulded into six 1x1x6-cm prismatic specimens and cured for 24 hours in a curing chamber (22 °C and 99 % relative humidity). The specimens were subsequently removed from the moulds and stored in the chamber until they reached the test age (2 or 28 days). The l/s ratio for each system was chosen to ensure that all the systems had a similar workability. A reserve sample was kept of both the activator-free binary and ternary blends for use as a reference.

At the specified ages, the specimens were tested to failure on an Ibertest (Autotest–200/10-SW) frame. Representative samples of the activated cementitious systems were selected for subsequent characterisation using X-ray diffraction (XRD), scanning electron microscopy (SEM/EDX) and (^{29}Si and ^{27}Al) nuclear magnetic resonance facilities. The XRD analyses were performed on a *BRUKER AXS D8 ADVANCE* diffractometer with a 4-kW high voltage generator and a Cu anode X-ray tube, typically operating at 40 kV and 50 mA. A *JEOL 5400* electron microscope fitted with an Oxford ISIS X-ray analyser was used for the SEM analyses. The NMR spectra were recorded on a Bruker Avance-400 spectrometer (^{27}Al: 104.3 MHz; spinning rate, 10 kHz; 200 acquisitions; reference, Al(H$_2$O)$_6^{3+}$; ^{29}Si: 79.5 MHz; spinning rate, 10 kHz; 1 000 acquisitions; reference, TMS).

3. RESULTS AND DISCUSSION

3.1 Mechanical Strength.

Figures 2(a) and (b) respectively show the compressive strength (MPa) findings for the 2- and 28-day binary (B2) and ternary (B3) binders.
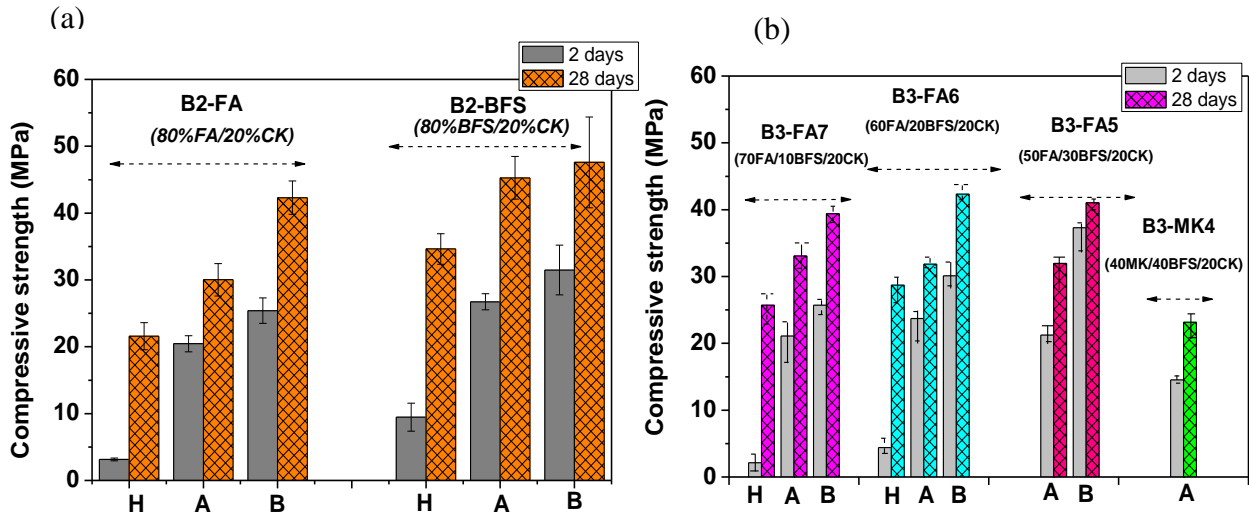

Figure 2. Compressive strength (MPa) values for 2- and 28-day (a) binary (B2) and (b) ternary (B3) binders [symbols: *H*=samples hydrated samples with no activator; *A*=samples activated with A; *B*=samples activated with B]

As Figure 2(a) shows, the presence of alkaline activators A and B, but especially B, enhances the development of mechanical strength. When these hybrid cements are alkali-activated, up to 80 % of the clinker can be replaced without affecting mechanical performance: both fly ash- and slag-containing binders exhibited 28-day compressive strength upward of 30 MPa.

When the binder consisting of a blend of high ash and low clinker contents is hydrated with water in the absence of activators, the clinker (20 % of the material) reacts first. The ash subsequently reacts with the $Ca(OH)_2$ precipitating during clinker hydration (pozzolanic reaction) ($C_3S+H_2O{\rightarrow}C$-S-H gel + $Ca(OH)_2$) (Taylor, 1997). Due to the low clinker and high ash content, this is a slow process. Hence the low early strength values. After reacting with water, the alkaline activator induces a rise in the aqueous phase pH, hastening fly ash dissolution. The higher pH values intensify reactivity and with it early strength values (García-Lodeiro et al., 2013a).

The process is similar in the system containing a blend of slag and ash. Moreover, since slag requires less aggressive activation conditions than ash, mechanical strength values were slightly higher in the slag- than in the ash-bearing hybrid cements. The alkaline medium activates the slag, generating a C-A-S-H gel that contributes to mechanical strength development in the system (Fernández-Jiménez et al., 2003).

The multi-component hybrid cements (ternary blends) studied also developed good cementitious properties (see Figure 2(b)). Mechanical strength exceeded 20 MPa in the 2-day systems containing variable proportions of ash and slag and 20 % clinker and rose to 32.5 MPa in the 28-day material (the requirement for commercial portland cements is 32.5 MPa). The highest strength values were attained with activator B in this case also. While the system consisting of

metakaolin, slag and clinker exhibited cementitious properties, the strength developed was lower than in the other binders.

These findings confirmed that the activators used in this study enhanced fly ash reactivity, with the formation of greater amounts of the cementitious gel that affords these materials their mechanical strength.

3.2. Mineralogical and Microstructural Characterisation.

Samples representative of the binary and ternary blends were selected for XRD, SEM/EDX and NMR analysis to study the reaction products generated.

3.2.1 Characterisation of binary blends

Figure 3(a) shows the XRD patterns for the 2- and 28-day B2-FA pastes and Figure 3(b) for the B2-BFS samples.

In system B2-FA (Figure 3(a)), all the diffractograms exhibited diffraction lines characteristic of quartz and iron oxides (minority mineralogical phases in the ash), as well as lines associated with calcite precipitation. The signal for alite (clinker) practically disappeared on the 28-day patterns in all the systems.

The pastes hydrated with water in the absence of activators (B2-FA-H) exhibited the 2-day behaviour expected: lines attributed to portlandite, which declined to near disappearance after 28 days as a result of the pozzolanic reaction.

Since the alkaline activators (both A and B) inhibited portlandite formation, however, this phase was not detected at either age in the systems hydrated in their presence. Moreover, ettringite was observed to precipitate much more significantly in the systems containing activator B.
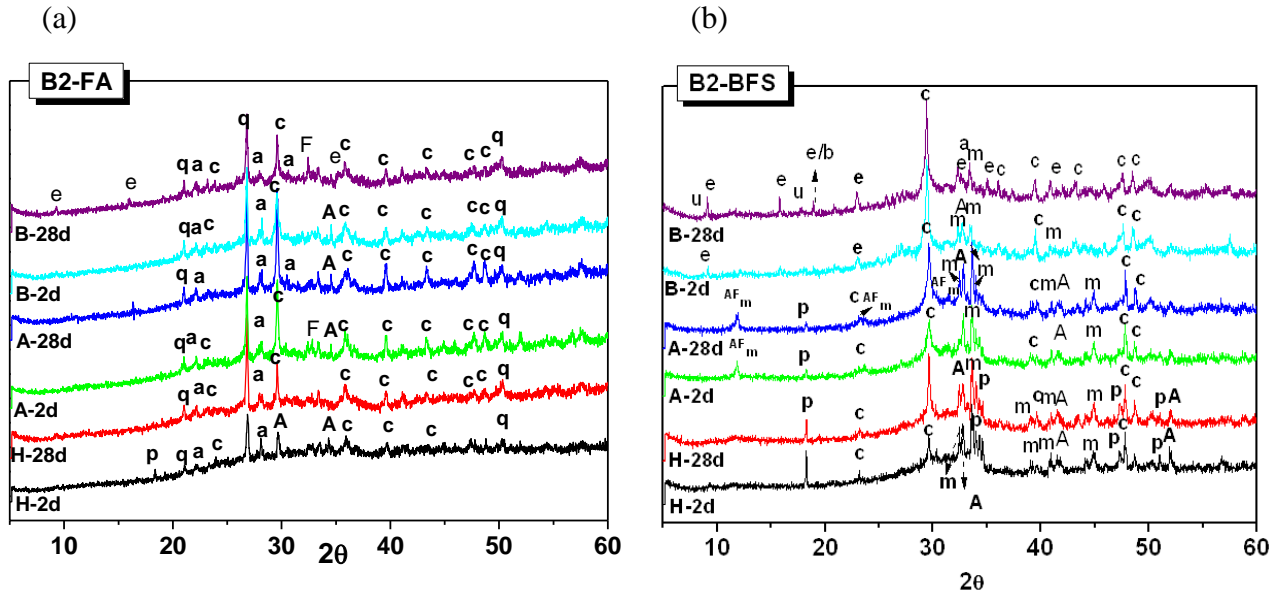
(a) (b)

Figure 3. Two- and 28-day diffractograms for (a) B2-FA and (b) B2-BFS pastes [symbols: *H=no activator; A=activator A; B=activator B; q=quartz (SiO_2); c=calcite ($CaCO_3$) ; a=anorthite; M=mullite ($3Al_2O_3.2SiO_2$); F=hematite (Fe_2O_3); m=merwinite ($Ca_3Mg(SiO_4)_2$); p=portlandite ($Ca(OH)_2$;·e=ettringite ($3CaO.Al_2O_3.3CaSO_4.32H_2O$); AFm =monocarboaluminate (C_4AcH_{11}); "phase u" =($3CaO.Al_2O_3.CaSO_4.0.5Na_2SO_4.15H_2O$)*]

Unreacted clinker was found in the blends containing clinker and slag (B2-BFS) (Figure 3(b)) with no activator (B2-BFS-H) and with activator A (B2-BFS-A). Portlandite was detected in both systems, although in greater amounts in the system hydrated in the absence of activators. In addition, both the 2- and 28-day A-activated materials exhibited a series of lines attributed to the precipitation of calcium carboaluminate hydrate, a compound normally observed in alkali-activated slag pastes (Fernández-Jimenez et al., 2013; García-Lodeiro et al., 2013b). Calcite was likewise identified in both systems.

The XRD patterns for system B2-BFS hydrated in the presence of activator B differed from the foregoing (see Figure 3(b)). In addition to calcite and ettringite, another calcium sulfoaluminate hydrate appeared, phase "u" (Arbi et al. 2013; Li et al., 1996).

The secondary products identified in systems hydrated in the presence of alkaline activators differ scantly from the ones traditionally detected in ordinary portland cement hydration (Lea, 1974; Taylor, 1997).

Lastly, all the XRD patterns also exhibited humps at 2Ɵ angles of 25-35º, attributed to the formation of a gel regarded as primarily responsible for the mechanical properties of these hybrid cements. Since this technique furnishes little information on gel composition and structure, however, some of the blends were chosen for SEM/EDX and (^{29}Si and ^{27}Al) MAS NMR analysis. A micrograph of 28-day, A-activated blend B2-FA is reproduced in Figure 4(a), along with the respective EDX. The micrograph in Figure 4(b) depicts the 28-day B2-BFS system hydrated in the presence of activator B.
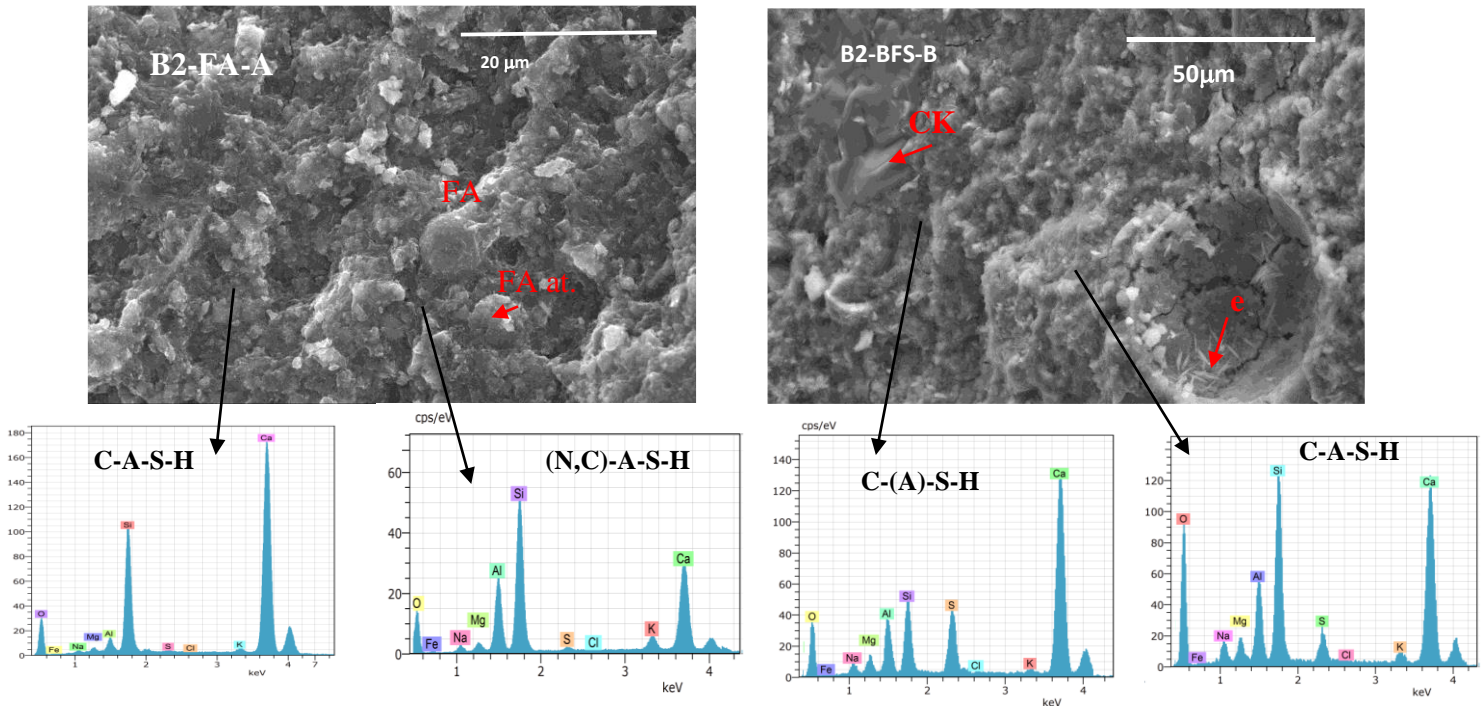

Figure 4. SEM micrographs showing the formation of cementitious gels (C-(A)-S-H, C-A-S-H and (N,C)-A-S-H) in and EDX analyses for (a) system B2-FA-A and (b) system B2-BFS-B [symbols: FA=fly ash; FA at.=fly ash under attack; CK=OPC clinker; e=ettringite]

System B2-FA had a compact matrix in which some of the ash particles had been attacked and others (covered with reaction product) had not. The precipitate observed contained a number of gels not morphologically distinguishable but with different chemical compositions (see EDX microanalysis, Figure 4(a)). Essentially two types of gels were present: one high in Ca, Si and Al (C-A-S-H, similar to the gel normally identified in ordinary cement hydration) and a more abundant Si- and Al-high gel containing Ca and Na ((N,C)-A-S-H), similar to the gel generated in the alkaline activation of fly ash.

System B2-BFS hydrated in the presence of activator B also exhibited a compact matrix (Figure 4(b)). Unlike the preceding system, however, here the primary reaction product was a C-A-S-H gel with C/S ratios of around 1 (see EDX microanalysis, Figure 4(b)). Gels with lower aluminium contents, known as C-(A)-S-H gels, also appeared sporadically. The micrograph further shows unreacted clinker particles and elongated interstitial crystals identified as ettringite needles (detected in the XRD analysis – see Figure 3(b)).

The evidence indicates that the chemical composition of the gels was largely conditioned by the chemical composition of the starting materials. Gels higher in calcium were generated in systems with a high calcium content such as B2-BFS, while silicon-rich gels were the major reaction product in systems high in silicon, such as B2-FA.

Figures 5(a) and (b) reproduce the 28-day ^{29}Si MAS-NMR and ^{27}Al MAS-NMR spectra for four versions of system B2-FA: anhydrous, hydrated with water only, activated by A, activated by B. The ^{27}Al and ^{29}Si spectra for system B2-BFS hydrated in the presence of activator B (B2-BFS-B) are also shown.

The ^{27}Al spectra for system B2-FA (Figure 5(a)) contained a wide signal at +52.7 ppm attributed to tetrahedral Al (Al_T), found essentially in the fly ash (Palomo et al., 2004; Fernández-Jiménez et al., 2006; Duxon et al., 2007). In light of the dilution involved (the binder contained 20 % clinker, whose Al_2O_3 content was just 4.85 %: see Table 1), portland clinker contribution to this signal was practically nil. When the binder was hydrated in the presence or absence of activators, the Al_T signal shifted slightly to +58 ppm and a signal associated with octahedral aluminium (AL_o) appeared between +5 and +10 ppm. As a technique highly sensitive to ^{27}Al nuclei, MAS-NMR is able to identify phases whose small quantity or poor crystallisation makes them nearly invisible to techniques such as XRD. The signal at around +10 ppm might be associated with the formation of calcium aluminate hydrates resulting from the hydration of the C_3A present in the clinker (in the absence of sulfates, logically). On the B2-BF-B spectrum, however, that signal shifted to +13.9 ppm, the position associated with the aluminium in ettringite (a phase detected with XRD: see Figure 3(a)). The shift in and narrowing of the Al_T signal observed in the hydrated materials may be associated with the dissolution of part of the Al present in the fly ash and its inclusion in the reaction products. Its position, at around +58 ppm, would indicate that this aluminium continued to be tetrahedral and to be surrounded by three or four silicon atoms.

The ^{27}Al spectrum for the slag system (B2-BFS-B) differed from the foregoing. Here the signal attributed to Al_T shifted toward more positive values, around +62 ppm, a position associated with the aluminium present in C-A-S-H gel (Richardson et al., 1997; Fernández-Jiménez et al., 2003). A very intense signal was also observed at +12.7 ppm, associated with the Al_o in the ettringite precipitate, also identified with XRD (see Figure 3(b)).

Interpretation of the ^{29}Si MAS-NMR for the system B2-FA (Figure 5b)) spectra is more complex. The intensity of the signal at -71.7 ppm (associated with the Q^0 units in the alite + belite present in the clinker) declined in all the hydrated materials, confirming that the calcium silicates in the clinker were reacting. The fly ash spectrum exhibited a wide signal centred at around -100 ppm. This signal contained a series of peaks at around -88, -100, -103 and -107 ppm, associated with

the various forms in which the silicate appeared in the fly ash (mullite, vitreous phase, quartz...) (Palomo et al., 2004; Fernández-Jiménez et al., 2006; Duxon et al., 2007). The intensity of the signals associated with the anhydrous phases declined in the spectra for the hydrated materials, while new (and intense) signals were found in the -80 to -100-ppm range. More specifically, the spectra for all the samples contained a strong signal at around --85 ppm that might be associated with Q^2 units (Andersen et al., 2003).
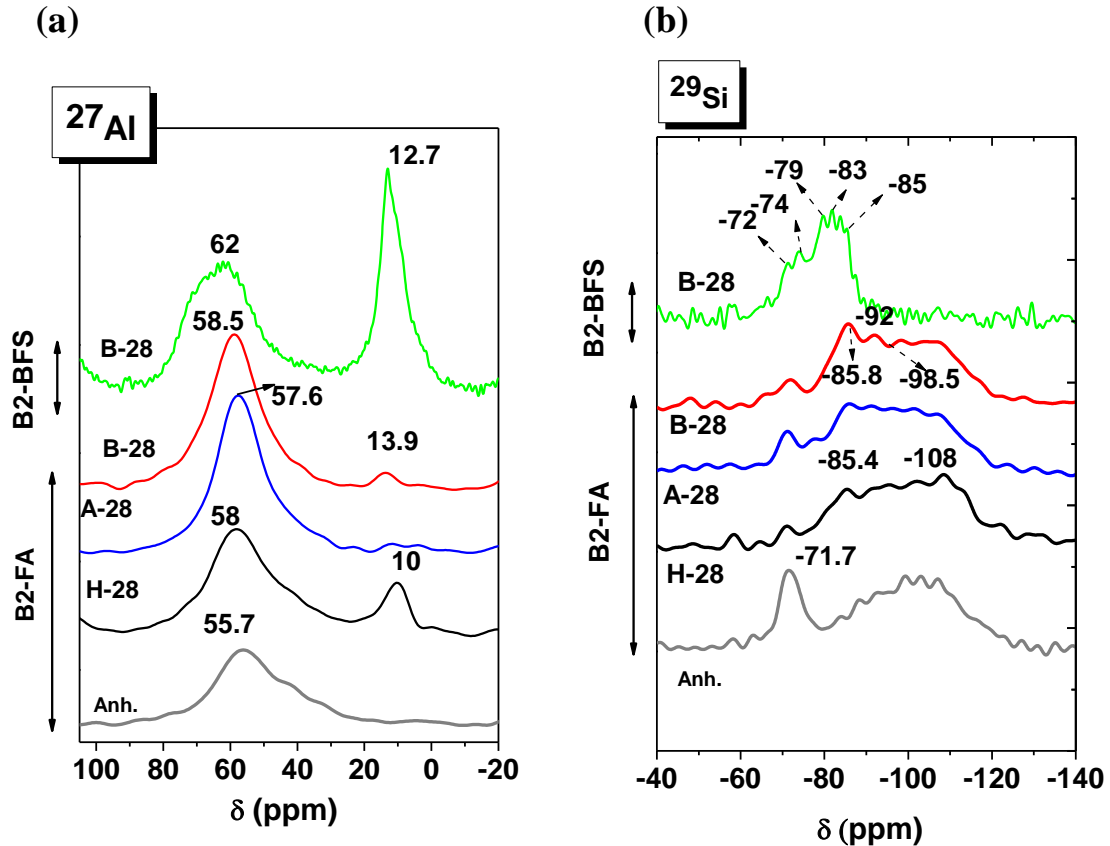

Figure 5. (a) ^{27}Al and (b) ^{29}Si MAS-NMR spectra for anhydrous system B2-FA and after hydration in the absence (H) and in the presence of solid activators A and B (A and B), and for system B2-BFS hydrated in the presence of activator B

The component associated with the presence of unreacted fly ash generated an intense signal (see the peak at -108 ppm on Figure 5(b)) on the spectrum for the binder hydrated in the absence of a solid alkaline activator (binder B2-FA-H), an indication that under these conditions the ash was scantly reactive. That would explain the low mechanical strength observed in this material. When solid alkaline activators were added (binders B2-FA-A and B2-FA-B), clearer signals were observed at -85 ppm, along with others at -92 and -98.5 ppm, particularly for binder B2-FA-B. These spectra proved to be very similar to the ones obtained for similar binders activated with liquid alkalis (Palomo et al., 2007). The increase in the signal at -85 ppm, along with the appearance of the new signals, denoted the formation of a more polymerised gel, consisting of $Q^3(nAl)$ or $Q^4(nAl)$ units. The presence of Al in positions at around +58 ppm was suggestive of the presence of $Q^4(4Al,)$, $Q^4(3Al)$ and $Q^4(2Al)$ units. The possibility of $Q^3(nAl)$ and $Q^4(nAl)$ signal overlapping cannot be ruled out, however.

The ^{29}Si spectrum for system B2-BFS-B differed from the foregoing. Here, in addition to the components at -72 and -74 ppm, respectively attributed to the Q^0 units in the clinker and the Q^1 units in the slag (Richardson et al., 1997), signals were observed at -79, -83 and -85 ppm, associated with Q^1, $Q^2(1Al)$ and Q^2 units, respectively, in C-A-S-H gel (Andersen et al., 2003). No signals for more polymerised units were detected, providing further evidence for the formation of a C-A-S-H gel in the system.

These findings appear to confirm that in the systems hydrated in the presence of a solid activator, the composition of the precipitates depended heavily on the raw materials. Two types of gels formed in the ash and clinker blend; i) a C-S-H gel with aluminium in its structure as a result of its reaction with the clinker; ii) a N-A-S-H gel with Ca in its structure as a result of the alkaline activation of the ash. The majority product in the slag and clinker blends was a C-A-S-H gel. The presence of solid activators raised ash and slag reactivity, furthering the precipitation of the cementitious gels that afford the system its good mechanical strength.

3.2.2 Characterisation of ternary blends.

Representative samples were chosen to analyse the reaction products generated in multi-component systems (ternary blends of the raw materials), namely blends B3-F6 (60 % FA + 20 % BFS + 20 % CK) and B3-MK4 (40 % MK + 40 % BFS + 20 % CK).

The diffractograms for system B3-FA6 hydrated for 2 and 28 days in the presence and absence of solid alkaline activators A and B are reproduced in Figure 6(a). The non-hydraulic crystalline phases present in the original raw material (slag and fly ash), including quartz, anorthite and iron oxides, were identified in the water-hydrated system. Portlandite was detected in the 2-day material, while alite and belite, the crystalline phases in anhydrous clinker, were barely perceptible, an indication that the portland clinker was hydrating normally. Portlandite was not present in the 28-day material, in all likelihood because it was consumed in the pozzolanic reaction described earlier, although carbonation ($Ca(OH)_2 + CO_2 \rightarrow CaCO_3$) cannot be ruled out. Calcium carbonate was detected at both ages.

The XRD patterns for the samples hydrated in the presence of solid activators And B differed from the foregoing (Figure 6(a)). In addition to quartz, hematite and anorthite, diffraction lines were identified for belite, particularly in the samples hydrated in the presence of activator A. The intensity of these lines declined with rising hydration time. Portlandite was not detected in any of the systems, although an AFm phase precipitated in one of the systems hydrated with activator A (B3-FA6-A-2), and ettringite in one hydrated with activator B.

As in the binary systems (B2), all the patterns exhibited an amorphous hump (2Θ=25-45°) associated with the formation of a gel.

The diffractograms for anhydrous B3-MK4, consisting of a blend of 40 % metakaolin + 40 % slag + 20 % clinker, and the same blend hydrated in the presence of activators A and B, are reproduced in Figure 6(b).

The systems hydrated in the presence of activator A generated diffraction lines attributed to the quartz and illite present in metakaolin. The intensity of the lines associated with the alite and belite in the anhydrous clinker declined or even disappeared altogether in the 28-day materials. Two calcium carbonate polymorphs, calcite and vaterite, were detected, along with the formation of the AFm phases identified in other blends (see Figures 6(a) and (b)) when activator A was used.

Activator B induced the formation of different secondary phases, in this case ettringite and other calcium sulfoaluminates (see Figure 6(b)). Calcium carbonate precipitated, along with the non-hydraulic mineralogical phases illite and quartz.
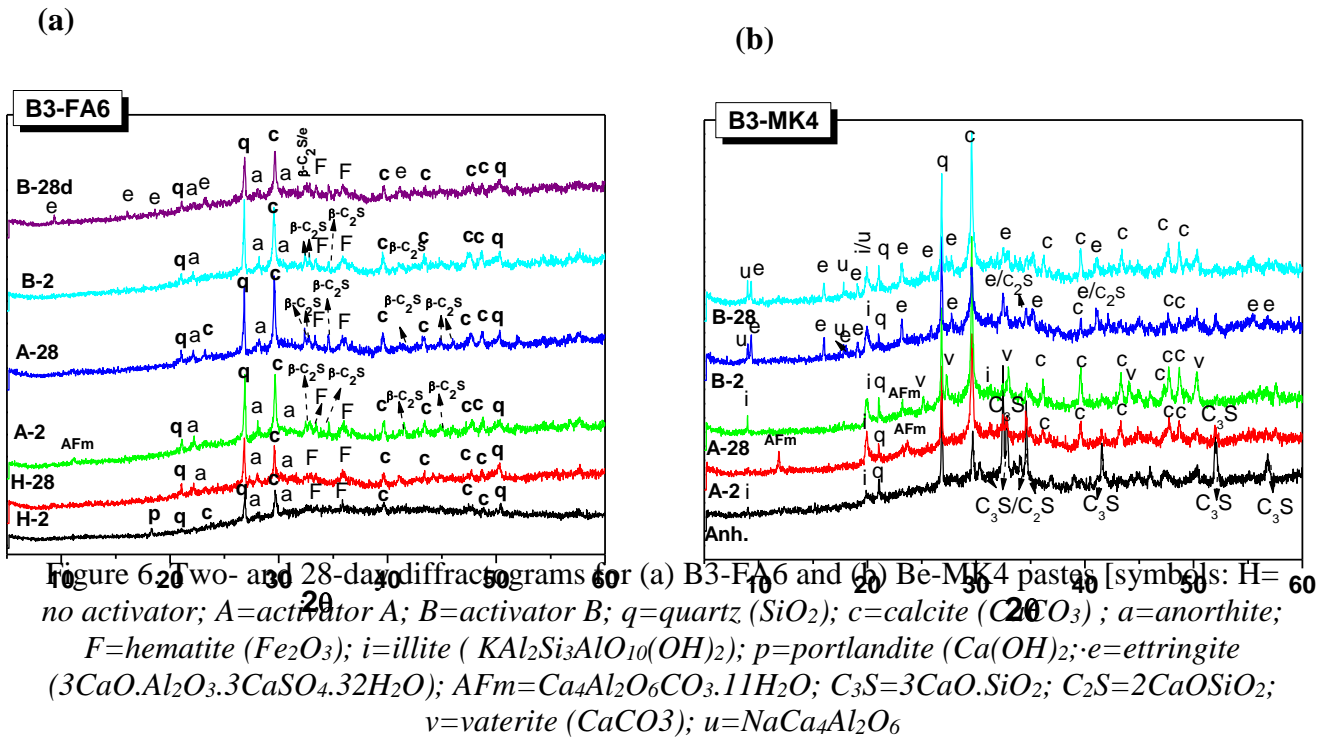
(a)

(b)

Figure 6. Two- and 28-day diffractograms for (a) B3-FA6 and (b) Be-MK4 pastes [symbols: H=
no activator; A=activator A; B=activator B; q=quartz (SiO_2); c=calcite ($CaCO_3$); a=anorthite;
F=hematite (Fe_2O_3); i=illite ($KAl_2Si_3AlO_{10}(OH)_2$); p=portlandite ($Ca(OH)_2$;·e=ettringite
($3CaO.Al_2O_3.3CaSO_4.32H_2O$); AFm=$Ca_4Al_2O_6CO_3.11H_2O$; C_3S=$3CaO.SiO_2$; C_2S=$2CaOSiO_2$;
v=vaterite ($CaCO3$); u=$NaCa_4Al_2O_6$
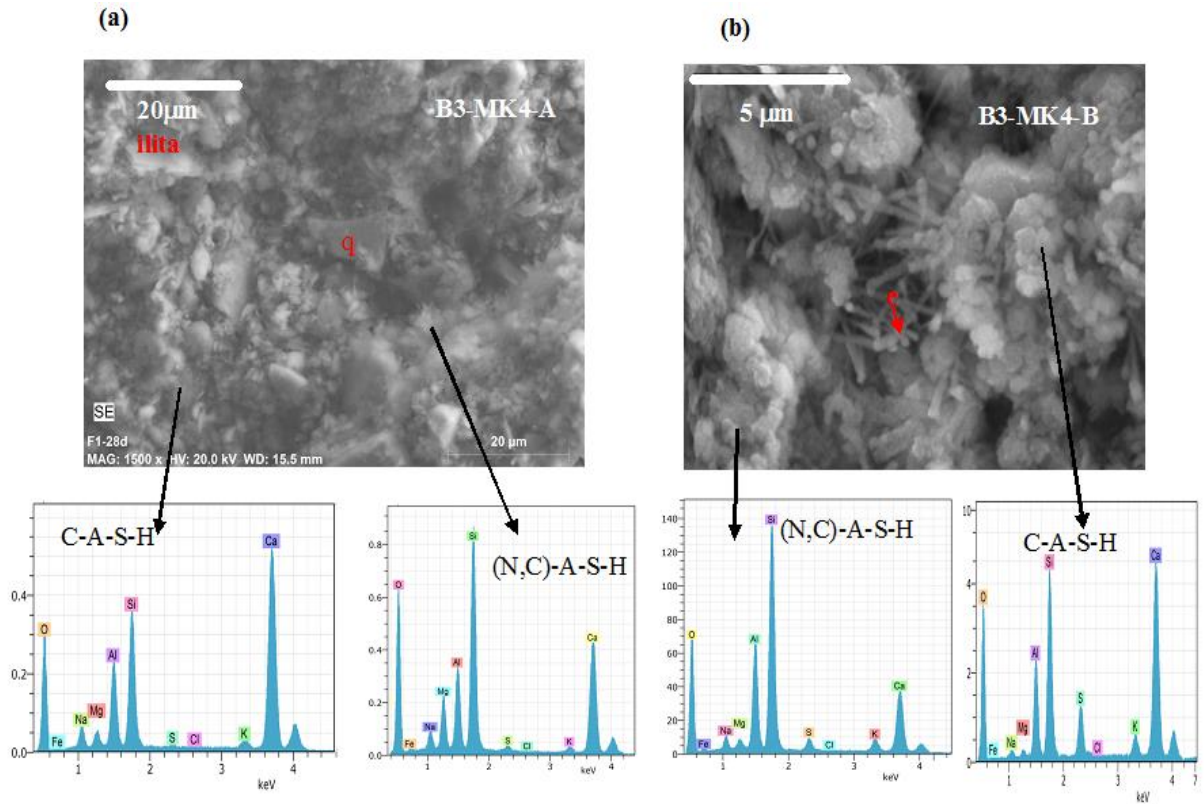
(a)

(b)

Figure 7. SEM micrograph and EDX analysis of (a) system B3-MK-A and (b) system BE-MK-B,
showing C-A-S-H and (N,C)-A-S-H cementitious gel formation [symbols: q=quartz; e=ettringite)

The amorphous hump detected here was also associated with a gel. Sample B3-MK4 hydrated in the presence of activators A and B for 28 days was selected for SEM/EDX analysis to study the gels generated in these multi-component systems.

According to the micrograph for system B3-MK-A (Figure 7(a)), a large amounts of a globular reaction product, which EDX analysis identified as a mix of C-A-S-H and (N,C)-A-S-H gels, precipitated. The matrix contained illite and quartz particles, but no anhydrous alite or belite.

The micrograph for system B3-MK4, hydrated in the presence of activator B (Figure 7(b)), shows the morphology of the precipitating gels in greater detail. As in the preceding system, both (N,C)-A-S-H and C-A-S-H gels were detected. The needles observed throughout the sample were ettringite crystals, a secondary phase identified on the XRD patterns (see Figure 6(b)). The findings suggested that the presence of activators A or B conditioned the type of secondary phases appearing in the hydrated systems: AFm when A was used and ettringite in the presence of B, although in both cases the main reaction product generated was a blend of (N,C)-A-S-H and C-A-S-H gels.

The nanostructure of the gels generated in these multi-component systems was analysed with MAS-NMR (^{27}Al and ^{29}Si). The systems chosen for analysis included one containing FA + BFS + CK (system B3-FA6) and one consisting of a blend of MK + BFS + CK (system B3-MK4).
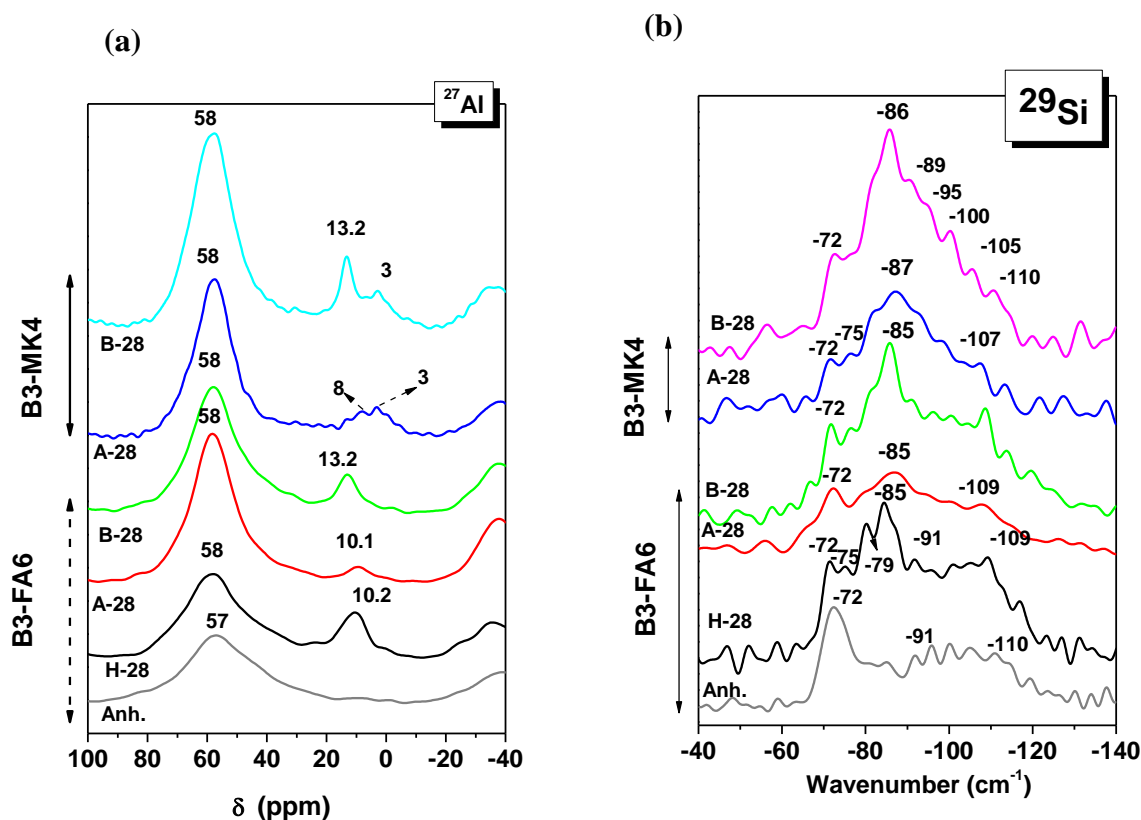

Figure 8. (a) ^{27}Al and (b) ^{29}Si MAS-NMR spectra for B3-FA6 and BK-MK4 [symbols: Anh. =anhydrous; H=hydrated for 28 days in the absence of activators; A=hydrated for 28 days with activator A; B=hydrated for 28 days with activator B]

The aluminium spectrum for anhydrous blend B3-FA6 (see Figure 8(a)) exhibited a single signal at +57 ppm, indicative of the presence of the tetrahedral aluminium found in the anhydrous ash and anhydrous slag both. Clinker contribution to that signal was practically nil due to the dilution effect. After the sample was hydrated in the presence and absence of the activator, the signal narrowed and shifted to +58 ppm. The AL_T signal that shifted with respect to the signal in the spectrum for the anhydrous blend was associated with the Al in the mix of C-A-S-H and (N,C)-A-S-H gels detected with SEM (see Figure 7(a)). A signal detected at around +10 ppm was attributed to the octahedral aluminium (Al_O) associated with carboaluminate formation. When activator B was used, the signal appeared at around +13.2 ppm, i.e., the position of the signal generated by the aluminium present in ettringite, whose presence had been detected with XRD (see Figure 3(a)).

The system containing metakaolin (B3-MK4) hydrated in the presence of activators A or B generated essentially two sets of signals: a first set located at around +58 ppm associated with Al_T (aluminium present in the reaction product, a mix of C-A-S-H and (N,C)-A-S-H gels) and a second located at lower chemical shift values, associated with Al_O. When the material was hydrated in the presence of activator A, two signals were observed for Al_O, one located at around +3 to +4 pm and the other at around +7 to +8 ppm, respectively associated in the literature with carboaluminate formation (AFm, detected with XRD) and the Al_O present in anhydrous metakaolin. Anhydrous metakaolin normally generates three signals, located at +55, +30 and +3 ppm, respectively attributed to tetra-, penta- and octahedral aluminium. The former two practically disappear during hydration (Fernández Jimenez et al., 2013).

In the presence of activator B, Al_O signals appeared in two positions, at around +13 ppm and at +3 to +4 ppm, again respectively associated with ettringite precipitation and unreacted metakaolin.

The interpretation of the ^{29}Si spectra (Figure 8(b)) is less straightforward, essentially because the bands generated by the many unreacted anhydrous components comprising these systems and by the hydration products overlap. The ^{29}Si spectrum for blend B3-FA6 exhibited an intense peak at -72 ppm, attributed to the Q^0 units in the clinker. A series of signals observed in the -91 to -110-ppm range was generated by the components present in the ash (vitreous phase, quartz, mullite...) discussed above in connection with the binary blends. The signal at around -74 ppm, typical of anhydrous slag and generated by Q^1 units, overlapped with the signal associated with the clinker, located at -72 ppm (Cong et al., 1996).

The spectra for the hydrated materials differed from the spectrum for the anhydrous blend. The sample hydrated exclusively with water exhibited signals at -79 and -85 ppm, characteristic of a C-S-H gel and respectively associated with units Q^1 and Q^2 (Andersen et al., 2003). A component detected at -75 ppm was attributed to the Q^1 units in the unreacted slag and a group of signals in the -91 to -109-ppm range to unreacted ash. A signal detected at -72 ppm was attributed to clinker, an indication that its calcium silicates (alite and belite) had not hydrated completely.

Hydration in the presence of both activators, but particularly B, modified the ^{29}Si spectra. The intensity of the signal for the clinker (-72 ppm) declined, while the other signals, at -85 ppm and in the -90 to -110-ppm range, intensified. These findings denoted the formation of more polymerised gels, i.e., consisting of Q^3(nAl) or Q^4(nAl) units, and were consistent with the shift in the Al_T signal for the hydrated phases.

The spectra generated by samples containing metakaolin (B3-MK4) differed from the foregoing, as described below. Both the A-28 and B-28 samples contained traces of clinker and unreacted slag. The most intense signal was located at around -86 to -87 ppm, suggesting the presence of more polymerised units, such as Q^3(nAl) or Q^4(nAl) (Engelhardt et al., 1987). Here also, the

interpretation of the signals in the -86 to -106-ppm chemical shift range was complex due to component overlapping (metakaolin also generates a wide, asymmetric band at around -108 ppm: Fernández-Jimenez et al., 2013), while the Al_T signal located at +58 ppm likewise suggested the presence of Q^4(nAl) units associated with the presence of a gel.

These results further confirmed that the activators used in this study enhanced supplementary cementitious material (fly ash, slag and metakaolin) reactivity, with the formation of greater amounts of the C-A-S-H + (C,N)-A-S-H cementitious gel to which these materials' good mechanical properties can be attributed.

4. CONCLUSIONS

Viable binders can be derived from cementitious materials with a very low (20 %) clinker content, providing they are hydrated in the presence of solid activators.

The alkaline activation procedure proposed here is applicable to different types and proportions of raw materials for the production of binders with good cementitious properties.

The main reaction product generated in the systems depends heavily on the chemical composition of the starting materials. Systems high in calcium (such as B2-BFS blends) generate primarily C-A-S-H gel. In systems with a higher silica and alumina content (such as B2-FA, B3-FA6 and B3-MK4), the main reaction product is a mix of C-A-S-H + (N,C)-A-S-H gels.

The use of one activator or another has no direct effect on the type of gels that precipitate, although it does condition the formation of secondary reaction products.

5. ACKNOWLEDGEMENTS

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