

Cements with low Clinker Content

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Abstract. Hybrid alkaline cements are multi-component systems containing a high percentage of mineral additions (fly ash, blast furnace slag), low proportions (<30 %) of Portland clinker and scarce amounts of alkaline activators. The substantially lower amount of clinker needed to manufacture these binders in comparison to ordinary Portland cement is both economically and ecologically beneficial. Their enormous versatility in terms of the raw materials used has made them the object of considerable interest. The present study explored the mechanical strength of binary blends mixes; B1= 20 % clinker (CK) + 80 % fly ash (FA) and B2=20 % clinker + 80 % blast furnace slag (BFS), both hydrated in the presence and absence of an alkaline activator specifically designed for this purpose. The use of the activator enhanced the development of early age strength considerably. All the hydrated matrices were characterised with XRD, SEM/EDX and (²⁹Si and ²⁷Al) NMR. The use of the alkaline activator generated reaction products consisting primarily of a mix of gels ((N,C)-A-S-H and C-A-S-H) whose respective proportions were found to depend upon system composition and initial reactivity.

1. Introduction

Portland cement is the material most widely used in construction today. Its mass production raises substantial energy and environmental issues, however. One of these issues is the manufacturing process, which entails the emission of greenhouse gases such as CO₂ and NO_x. With 0.8 tonnes of CO₂ per tonne of cement manufactured, the industry accounts for 7-8 % of worldwide emissions of this greenhouse gas [1].

One of the approaches 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) widely accepted today is to include active industrial by-product or mineral additions in Portland cement clinker. Another more innovative option consists of developing alternative, less expensive and where possible less environmentally damaging cements (involving lower CO₂ 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

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known as “*alkaline cements*” [2-4]. *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. Based on the nature of the cementitious components, alkaline cements can be grouped under different categories. One of such categories is a new type of binder known as *hybrid alkaline cements*, formed as a result of alkaline activation of materials with low Portland cement clinker (from 0 to 30 %) and high proportions of mineral additions (slags, fly ash, metakaolin, etc.).

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

2.1. Materials

The raw materials used included a commercial clinker (CK) supplied by a Spanish cement factory, granulated blast furnace slag (BFS), (from Algeria) and a Slovakian type F fly ash (FA). The chemical composition of the materials given in table 1 was determined by XRF on a PHILIPS PW-1004 X-ray spectrometer. Their mineralogy (XRD-determined) is shown in figure 1.

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

	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	MgO	Na ₂ O	SO ₃	K ₂ O	TiO ₂	P ₂ O 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

*LOI: Loss on ignition (1000°C)

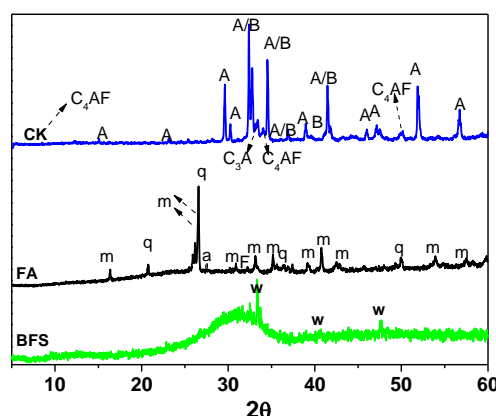


Figure 1. XRD patterns of Raw materials (CK: clinker; FA: Fly Ash; BFS: Blast Furnace Slag) (Legend: A: alite (C₃S); B: belite (C₂S); C₃A: tricalcium aluminate; C₄AF: ferrite phase; q: quartz (SiO₂); m: mullite (3Al₂O₃·2SiO₂); F: hematite (Fe₂O₃); a; anorthite; w=merwinite (Ca₃Mg (SiO₄)).

2.2. Methodology

Two binders were prepared; **B1** consisting of a blend of 20 % clinker and 80 % fly ash and **B2** consisting of a blend of 20 % clinker and 80 % blast furnace slag. The binders included 4% of solid Na_2CO_3 as alkaline activator (see table 2). 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 and 28 days). The w/c ratio for each system was chosen to ensure that all pastes had similar workability. A reserve sample (activator-free) of both blends was kept for use as a reference.

Table 2. Binder composition.

FA	BFS	CK	Activator*	Liquid of hydration	w/c**	Nomenclature
80	--	20	--	water	0.40	B1W
80	--	20	Na_2CO_3	water	0.38	B1A
--	80	20	--	water	0.26	B2W
--	80	20	Na_2CO_3	water	0.26	B2A

*As all the alkali activated blends contained 4 % of Na_2CO_3 , the end product contained 96 % of binder and 4 % activator

** water/cement ratio

The specimens were tested to failure on an Ibertest (Autotest–200/10-SW) frame. Hybrid cements were characterised with XRD, SEM/EDX and ^{29}Si and ^{27}Al NMR. The XRD data were acquired with 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 Jeol5400 electron microscope fitted with an OxfordISIS 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, $\text{Al}(\text{H}_2\text{O})_6^{3+}$; ^{29}Si : 79.5 MHz; spinning rate, 10 kHz; 1 000 acquisitions; reference, TMS).

3. Results and Discussion

3.1. Mechanical Strength Behaviour

Figure 2 shows the compressive strength (MPa) findings for the 2- and 28-day binders. The presence of alkaline activator 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 exceeding 30 MPa.

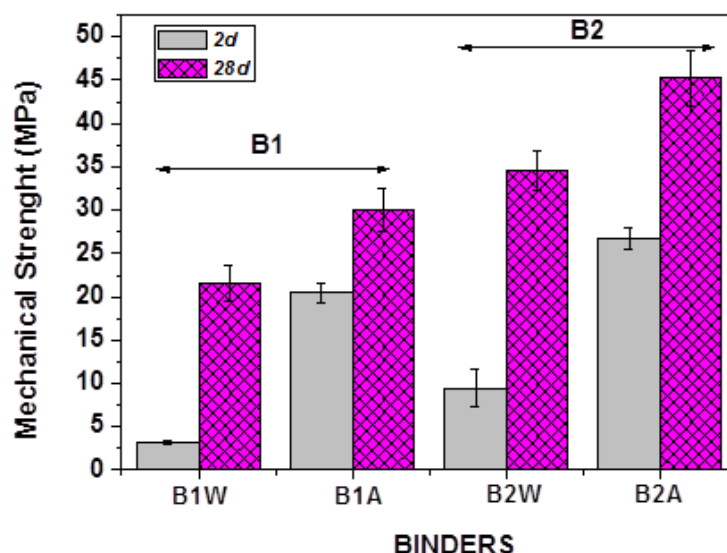


Figure 2. Compressive strength behaviour (MPa) for 2- and 28-day binders (**B1**: 80% FA+20% CK; **B2**: 80% BFS+20% CK; **W**: samples hydrated with no activator; **A**: samples activated with Na_2CO_3).

When the binder consisting of a blend of high ash and low clinker content (*B1*) is hydrated with water in the absence of activators, clinker (20 % of the material) reacts first. Ash, subsequently, reacts with $\text{Ca}(\text{OH})_2$ formed during clinker hydration (pozzolanic reaction) ($\text{C}_3\text{S} + \text{H}_2\text{O} \rightarrow \text{C-S-H gel} + \text{Ca}(\text{OH})_2$) [5]. Due to low clinker and high ash content, this is a slow process. Hence, the low early strength development. In presence of an alkaline activator, this induces a rise in the aqueous phase pH, hastening fly ash dissolution. Higher pH values intensify reactivity and along with it early strength values (see figure 2) [6].

The process is similar in the system B2 containing slag. 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 [7].

3.2. Characterization of different binders

Figures 3(a) and (b) show respectively the XRD patterns for the 2- and 28-day B1 and B2 binders. In system B1 (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 activator (B1W) 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.

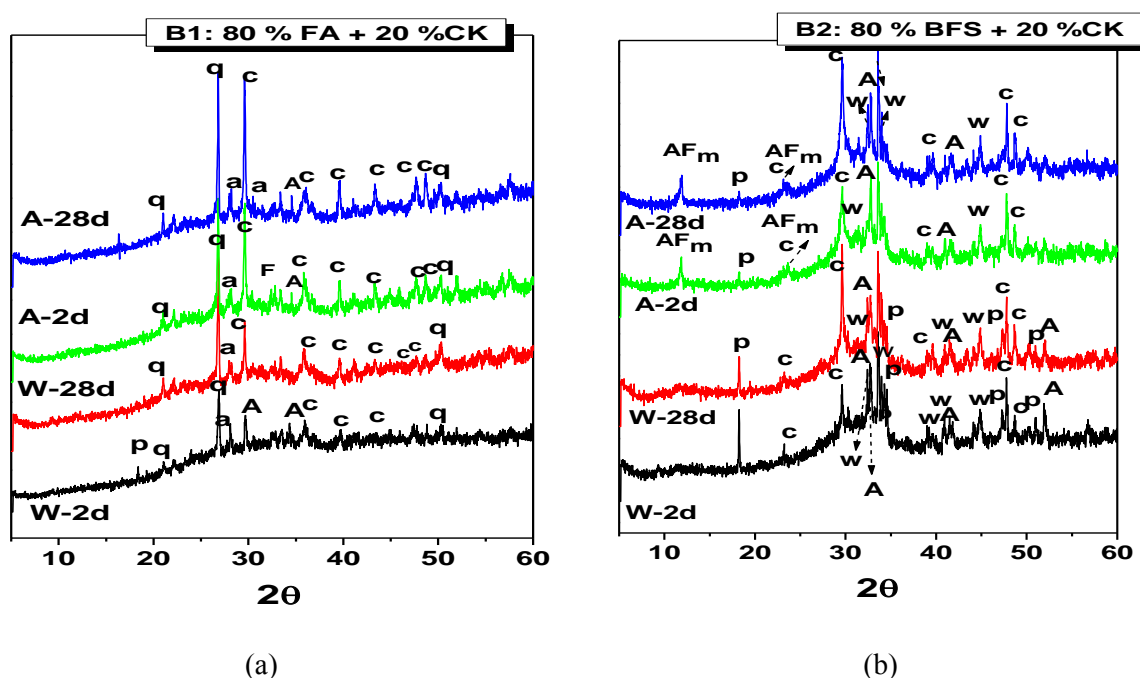


Figure 3. XRD patterns of (a) **B1 Binders** (80 %FA + 20 % CK) (b) **B2 Binders** (80 % BFS + 20 % CK) (Legend: c: Calcite (CaCO₃); p:portlandite (Ca(OH)₂); AFm: monocarboaluminate (C₄A·H₁₁)).

Unreacted clinker was found in the blends containing clinker and slag (B2) (figure 3(b)) with no activator (B2W) and with activator A (B2A). 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 activated materials exhibited a series of lines attributed to the precipitation of calcium carboaluminate hydrate (AFm), a compound normally observed in alkali-activated slag pastes [8-9]. Calcite was likewise identified in both systems. All the XRD patterns also exhibited humps at 2θ angles of 25-35°, 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, some of the alkali activated blends (B1A and B2A, at 28 days) were chosen for SEM/EDX and (²⁹Si and ²⁷Al) MAS NMR analysis.

System B1A had a compact matrix in which some of the ash particles had been attacked and others (covered with reaction product) had not (see figure 4(a)). 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 rich in Ca, Si and Al (C-A-S-H gel¹, 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 gel¹), similar to the gel generated in the alkaline activation of fly ash.

¹C: CaO; S: SiO₂; A: Al₂O₃; N: Na₂O; H: H₂O

System B2A 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 previously observed by XRD (see figure 3(a)).

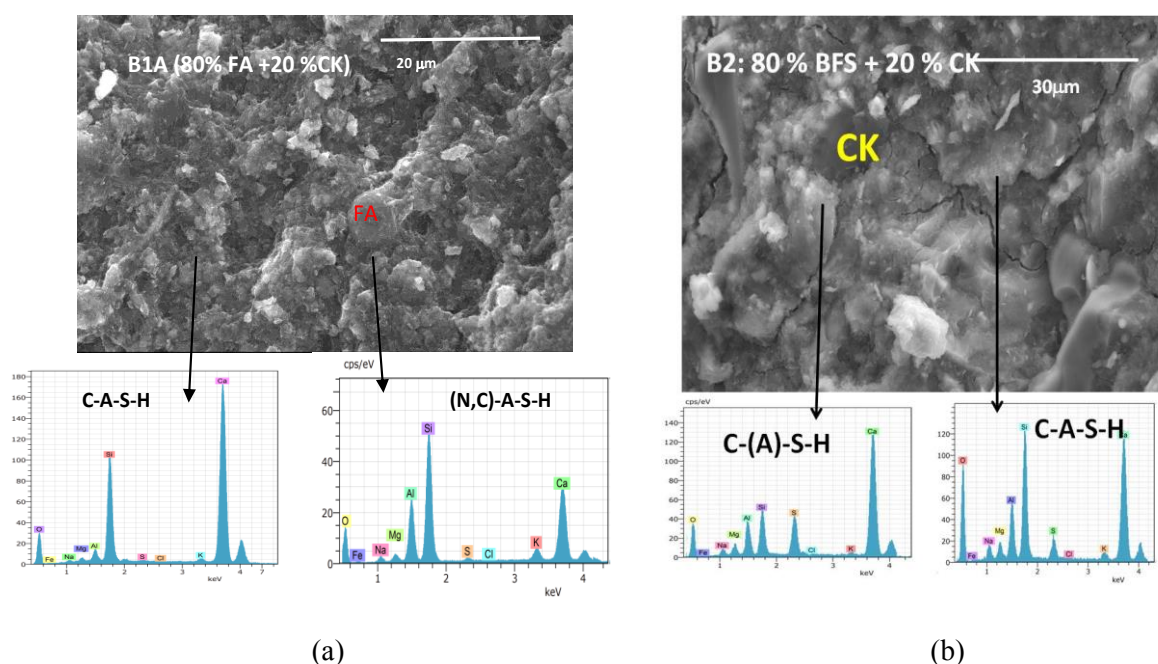


Figure 4. SEM micrographs at 28 days of (a) B1A and (b) B2A binders, where we can differentiate the precipitation of C-(A)-S-H, C-A-S-H and (N,C)-A-S-H gels (EDX analyses).

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 the systems with high calcium content such as B2 (80 %BFS + 20 %CK), while silicon-rich gels were the major reaction product in the systems high in silicon, such as B1 (80 % FA + 20 %CK).

Figures 5(a) and (b) reproduce the 28-day ^{27}Al MAS-NMR and ^{29}Si MAS-NMR spectra for system B1: raw materials involved in the blend (CK and FA), B1 hydrated with water only (B1W) and alkali activated by Na_2CO_3 (B1A). Figures 5(c) and (d) reproduce the analogous spectra for B2 system (including the spectra associated with CK and in this case BFS).

If we focus our attention on figures 5(a) (^{27}Al spectra), clinker phase shows a narrow signal located at +80 ppm associated with tetrahedral aluminium (Al_T), while anhydrous FA shows a broad and asymmetrical signal located at +56 ppm also attributed to tetrahedral Al (Al_T) [10-12]. When the binder was hydrated in the presence or absence of activator, 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. 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 surrounded by three or four silicon atoms.

The ^{27}Al spectrum for the slag system (B2) differed from the foregoing (see figure 5(c)). 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 [7,13]. A very intense signal was also observed at +12.7 ppm, associated with the Al_0 in the AFm phase precipitate, also identified with XRD (see Figure 1(c)). Interpretation of ^{29}Si MAS-NMR for the system B1 (figure 5(b)) spectra is more complex. The intensity of the signal at -71 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 -109 ppm. This signal contained a series of peaks at around -88, -100, -103 and -110 ppm, associated with the various forms in which the silicate appeared in the fly ash (mullite, vitreous phase, quartz, etc.) [10-12]. 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/-86 ppm that might be associated with Q^2 units [14].

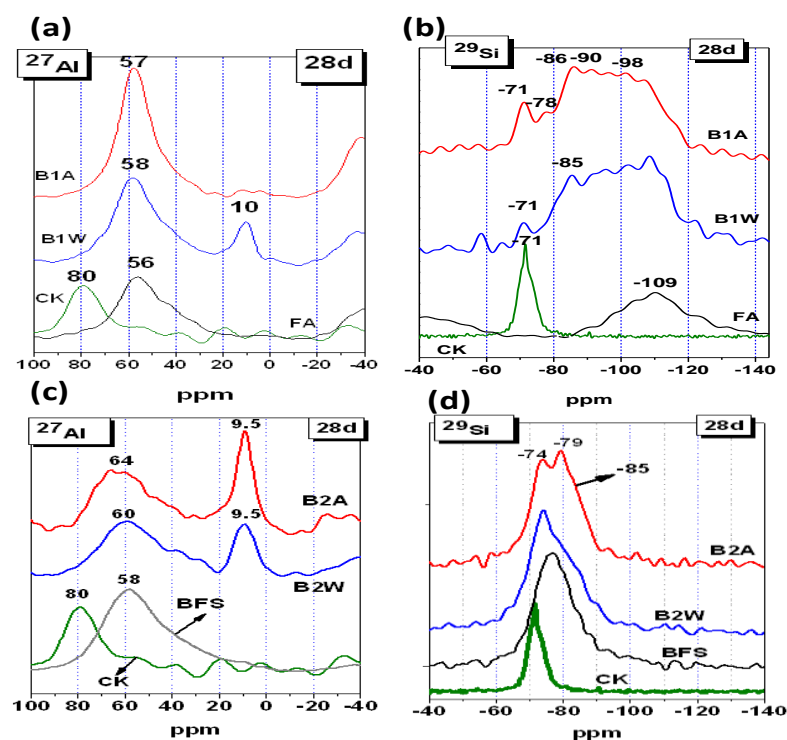


Figure 5. (a) ^{27}Al and (b) ^{29}Si MAS-NMR spectra for **B1 binders** (at 28 days) and (c) ^{27}Al and (d) ^{29}Si MAS-NMR spectra for **B2 binders** (at 28 days).

The component associated with the presence of unreacted fly ash generated an intense signal (see the peak at -110 ppm on figure 5(b)) on the spectrum for the binder hydrated in the absence of a solid alkaline activator (B1W), an indication that under these conditions the ash was scantily reactive. That would explain the low mechanical strength observed in this material (see figure 2). When solid alkaline activator was added (B1A), cleared signals were observed at -79 ppm and -86 ppm (which can be associated with Q^1 and Q^2 units in C-S-H gel), along with other signals at -90 and -98.5 ppm. These spectra proved to be very similar to the ones obtained for similar binders activated with liquid alkalis [15]. The increase in the signal at -85 ppm, along with the appearance of 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, associated with N-A-S-H gel precipitation. The possibility of $Q^3(nAl)$ and $Q^4(nAl)$ signal overlapping cannot be ruled out, however.

The ^{29}Si spectrum for system B2 differed from the foregoing (see figure 5(d)). Here, in addition to the components at -71 and -74 ppm, respectively attributed to the Q^0 units in the clinker and the Q^1 units in the slag [13], 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 [14]. No signals for more polymerised units were detected, providing further evidence for the formation of 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 (B1A and B2A), 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 (B1A); 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 (B2A) was C-A-S-H gel. The presence of solid activators raised reactivity of ash and slag, furthering the precipitation of the cementitious gels that ensure good mechanical strength of the system.

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 alkaline activators.
- The alkaline activation procedure proposed here is applicable to different types 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 80 % BFS + 20 % CK blends) generate primarily C-A-S-H gel. In systems with higher silica and alumina content (such as 80 % FA + 20 % CK), the main reaction product is a mix of C-A-S-H + (N,C)-A-S-H gels.

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