CIMENTURI HIBRIDE ALCALINE. PARTEA a II-a: FACTORUL CLINCHER▲
HYBRID ALKALINE CEMENTS. PART II: THE CLINKER FACTOR

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    The binders known as blended or hybrid alkaline cements are obtained by alkali-activating cementitious blends in the Na_2O-CaO-SiO_2-Al_2O_3-H_2O system. The present paper discusses the results of alkali activating blends prepared were: binder BSLAG = 20 % OPC clinker + 80 % BFS; and binder BFA = 20 % OPC clinker + 80 % FA. The 2-day mechanical strength was over 15 MPa. The main reaction products were gels whose composition varied depending on the initial Ca content. In alkali-activated BSLAG cement they consisted of a mix of C-S-H/C-A-S-H and in activated BFA cement of a mix of C-A-S-H /(N,C)-A-S-H.

    Lianţii cunoscuţi ca cimenturi amestecate sau cimenturi alcaline hibride, sunt obţinuţi prin activarea alcalină a amestecurilor cimentoide în sistemul Na_2O-CaO-SiO_2-Al_2O_3-H_2O. În acest articol sunt caracterizate cimenturile amestecate activate alcalin, preparate astfel: liantul pe bază de zgură bazică de furnal (BSLAG) = 20% OPC clincher + 80% zgură (BFS) şi liantul pe bază de cenuşă zburătoare (BFA) = 20% OPC clincher +80% cenuşă zburătoare (FA). Rezistenţa la compresiune la 2 zile a fost de peste 15 MPa. Produşii de reacţie principali, de tip gelic, au avut o compoziţie determinată de conţinutul iniţial de Ca. Compoziţia liantului BSLAG constă din C-S-H şi C-A-S-H, iar liantul BFA se caracterizează prin C-A-S-H şi (N,C)-A-S-H.

1. Introduction

    Portland cement-based concrete is today's construction material per excellence. It owes this pre-eminence to its mechanical strength, high value for money and generally good performance. Nonetheless, portland cement manufacture is energy-intensive (calling for temperatures of up to 1400-1500 ºC) and has a heavy environmental footprint (extraction of raw materials with the concomitant destruction of natural quarries and emission of GHGs such as CO_2 and NO_x) [1]; for every tonne of cement manufactured, approximately 0.8 tonnes of CO_2 are released into the atmosphere, contributing substantially to global air pollution (the cement industry accounts for 5 to 8 % of world-wide CO_2 emissions).

    The reduction of the portland cement content in construction binders via replacement with supplementary cementitious materials (SCMs) such as slag, natural pozzolans or fly ash is a successful practice that has been in place for many years [2]. The use of SCMs has, moreover, been acknowledged by legislation the world over as a way of generating different types of cement and consolidated by unanimous reports that it leads to significant improvements in cementitious systems while contributing to sustainability.

    One of the more innovative solutions to these problems, which also yields a better environmental balance (with the re-use of industrial by-products or waste whose stockpiling is costly and induces pollution), consists of developing alternative binders, if possible more respectful of the environment (lower CO_2 emissions, re-use of industrial by-products), less expensive and with similar or even better performance than ordinary portland cement. One such option is to be found in a series of materials with cementitious properties that are generically known as *"alkaline cements"* [3-5].

    Alkaline cements are binders formed when SiO_2- and Al_2O_3-rich natural or industrial waste materials (aluminosilicates) with amorphous or vitreous structures are dissolved in an alkaline medium. When so dissolved and after brief thermal activation, these aluminosilicates can set and harden to produce a material with good cementitious properties. Recent 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"* [6-10].

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The present study focused on alkaline activation as an effective procedure for reducing the clinker content in cements with good mechanical performance. It explored process kinetics and the mechanical, mineralogical and microstructural properties of the *hybrid cements* prepared (20 % Portland clinker and 80 % fly ash, a calcium-poor industrial by-product, or calcium-rich blast furnace slag).

2. Experimental

The materials used in the present research were clinker, type F fly ash and blast furnace slag.

The chemical composition (found with a PHILIPS PW-1004 X-RAY spectrometer) of these materials and of the binders prepared, BFA and BSLAG, is given in Table 1.

The blends were hydrated with water in the presence or absence of an alkaline activator. The water/binder ratios used in each case are given in Table 2. The pastes obtained were moulded into 1x1x6-cm prismatic specimens and cured for 24 hours in a curing chamber (22 ºC 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).

Table 1

Chemical composition (wt%) / *Compoziția chimică (%)*

	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	Na_2O	SO_3	K_2O	TiO_2	P_2O_5	LoI[3]
Clinker / *Clincher*	21.83	4.85	61.19	3.20	2.03	0.69	1.11	1.76	0.15	0.48	2.65
Fly ash / *Cenuşă zburătoare*	56.51	21.42	3.78	8.57	2.19	0.63	0.99	2.59	0.87	0.15	2.21
Slag / *Zgură*	36.63	7.25	38.09	0.46	8.51	0.53	2.13	0.62	0.27	0.06	4.88
[1]BFA	49.56	18.10	15.25	7.50	2.15	0.64	1.01	2.42	0.72	0.216	2.30
[2]BSLAG	33.68	6.77	42.77	1.01	7.21	0.56	1.93	0.53	0.25	0.14	4.43

[1]BFA, Binder =20 % portland clinker +80 % fly ash, [2]BSLAG =20 % portland clinker +80 % slag, [3]LoI =loss on ignition at 1000 ºC
[1]BFA, Lisant =20 % clincher portland +80 % cenuşă zburătoare, [2]BSLAG =20 % clincher portland +80 % zgură, [3]LoI = pierdere la ardere la 1000 ºC

Table 2

Hybrid cement characteristics and setting times / *Caracteristicile compoziționale şi priza cimenturilor hibride*

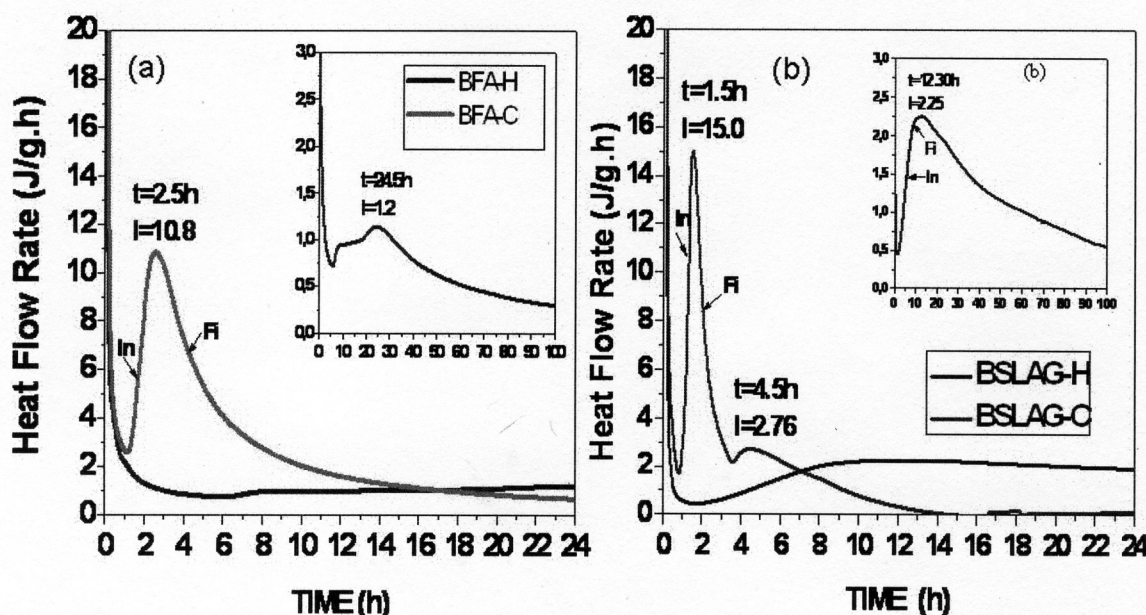| Name / *Nume*	Activator / *Activator*	Water/binder ratio / *Raport apă/liant*	Setting time / *Timp de priză*	
			Initial (In)	End (Fi)
BFA-H	No	0.38	< 18h	?
BFA-C	Yes	0.38	1h 47 min	4h 12 min
BSLAG-H	No	0.26	6h 12 min	9h 12min
BSLAG-C	Yes	0.26	1h 25mim	2h 8min

Fig. 1 - Heat flow curves: (a) BFA samples; (b) BSLAG samples; In = initial and Fi =final setting time/ *Curbe de încălzire: (a) probe BFA; (b) probe BSLAG ; In = timpul initial şi Fi =timpul final de priză.*

The specimens were tested to failure on an Ibertest (Autotest –200/10-SW) test frame. After these trials, part of the material was ground (to < 45 μm) and subsequently frozen with an acetone/ethanol mix to detain hydration. This material was characterised by XRD on a *BRUKER AXS D8 ADVANCE* diffractometer fitted with a 4-kW high voltage generator and a Cu-anode X-ray tube whose standard operating settings were 40 kV and 50 mA. The NMR studies were conducted with a BRUKER AVANCE-400 spectrometer.

The setting times were defined as specified in Spanish and European standard UNE-EN 196-3:2005+A1:2009. Reaction kinetics were studied in 5-g samples of binder mixed with water at the same liquid/solid ratio as used in the pastes (see Table 2) on a TAM Air *THERMOMETRIC 3116/3239* conduction calorimeter. The test temperature was a constant 25 ±0.5 °C.

3. Results and discussion

Figure 1 shows the heat flow curves obtained with isothermal conduction calorimetric. The ascending arm of the pre-induction peak was not detectable in any of the specimens, although the descending arm, the induction period and the acceleration-deceleration peak associated with mass reaction product precipitation were clearly visible. The presence of the alkali activator in the medium accelerated reaction kinetics considerably in both blends and raised the intensity of the heat flow peak. In the presence of the alkaline activator, the material containing slag (BSLAG-C) (Fig. 1(b)) exhibited a more intense peak at somewhat shorter times than the fly ash blend (BFA-C) (Fig. 1(a)). Another significant finding was the presence of a third signal at 4.5 hours with an intensity of 2.76 J/g.h in the BSLAG-C blends.

In both cements, the presence of the activator shortened setting times, especially in the case of binder BFA. In normal Portland cement pastes, initial and setting time concur with the initial and final acceleration peak on the hydration heat flow curves [11], which is associated primarily with the formation of a calcium silicate hydrate such as C-S-H gel. Here, however, when setting times were compared to the heat flow curves, slight differences were observed in both the BFA-C and BSLAG-C systems. In these materials, while initial setting concurred with the beginning of the acceleration peak, end setting time was longer and instead of concurring with the tip of the, was located on the descending arm, i.e., during deceleration (See Table 2). This might be due to a series of interactions between the products released during Portland cement clinker hydration and the substances formed during the fly ash or slag reaction.

Figure 2 shows the compressive strength development for the two cements prepared with and without the alkaline activator, whose presence clearly induced a substantial rise in binder mechanical strength, particularly at the earliest ages. The highest 2-day strength values were observed for cement BFA-C. After 28 days, however, cement BSLAG, with or without the alkaline activator, exhibited the highest compressive strength values.
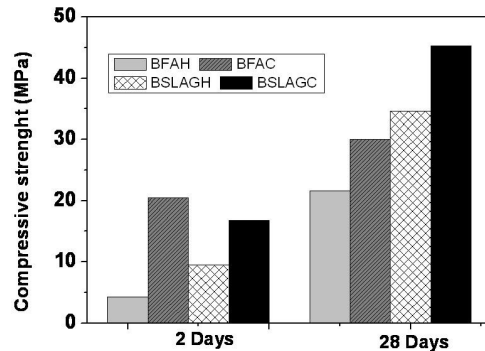
Fig. 2 - Compressive strength/ *Rezistența la compresiune.*

3.1. Characterization

Figure 3 shows the XRD patterns for the starting materials. The patterns exhibited the mineralogical phases typically present in clinker (alite, belite, C_3A, brownmillerite) and the high vitreous content (see halo at 25-35°) in the slag, and revealed that merwinite was the minority phase in this material. The vitreous content in the fly ash (halo at 20-30°) was observed to be similarly high and its minority crystalline phases were quartz, anorthite, mullite and Fe_2O_3.

Fig. 3 - XRD patterns showing mineralogical phases in the starting materials / *Difractogramele RX cu fazele mineralogice din compoziția materialelor inițiale.*
Legend: *Q=quartz;; a=anorthite; M=mullite; Fe=hematite; m=merwinite ($Ca_3Mg(SiO_4)_2$). A=alite; b=belite; d=C_3A; B=brownmillerite.*

Fig. 4 - Two- and 28-day XRD traces: (a) cement BFA; (b) cement BSLAG / *Difractogramele RX caracteristice pentru paste la 2 zile şi la 28 zile: a) ciment BFA; (b) ciment BSLAG.*
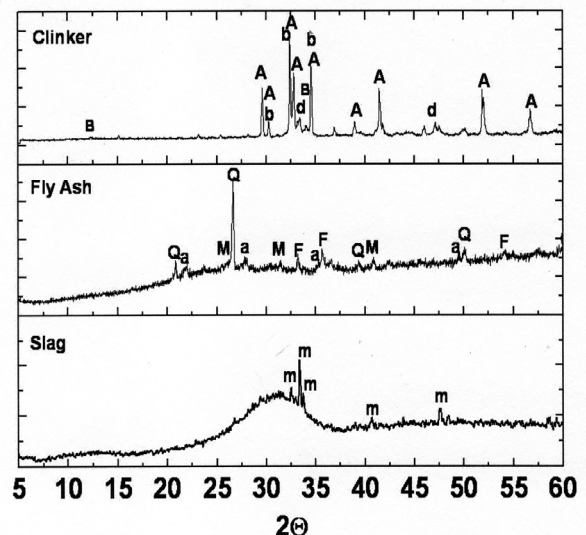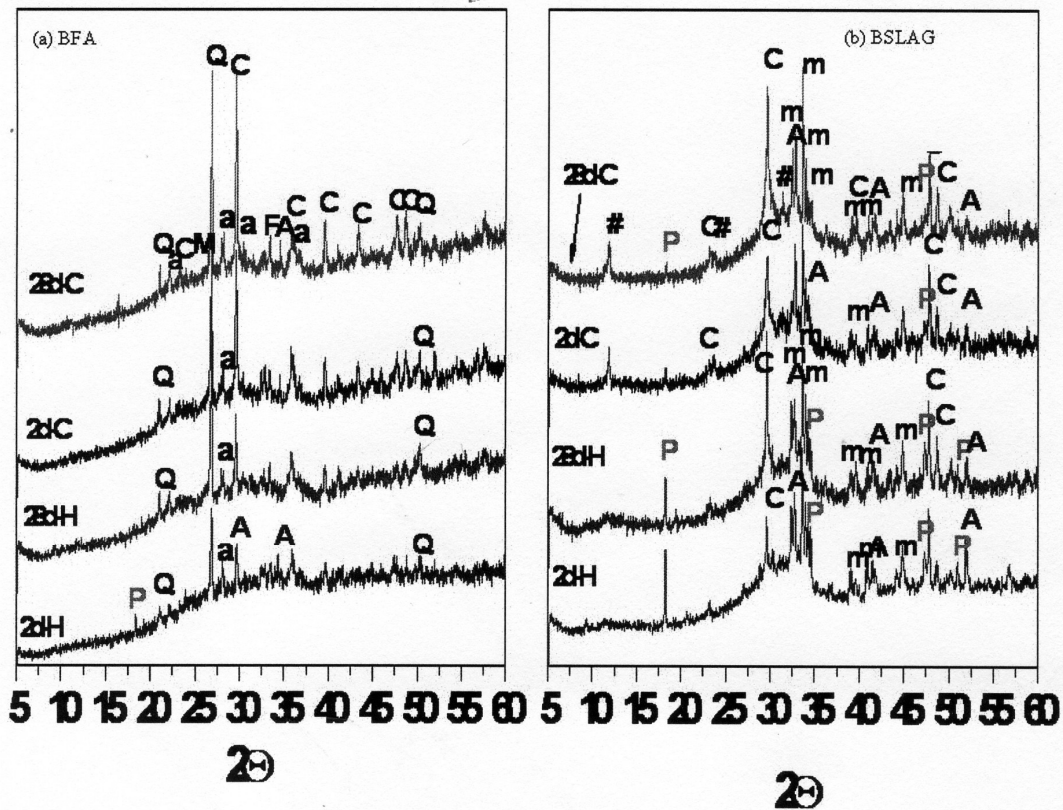**Legend:** *Q=quartz; C=calcite; a=anorthite; M=mullite; Fe=hematite; m=merwinite (Ca₃Mg(SiO₄)₂; .P=portlandite;·# =monocarboaluminate (C₄AcH₁₁).*

Figure 4 shows the XRD patterns for the 2- and 28-day pastes. The findings for the pastes hydrated in the absence of alkalis were as expected: the portlandite observed in the 2-day material was largely consumed after 28 days as a result of the pozzolanic reaction, especially in BFA-H systems. Moreover, the portlandite content was lower in the fly ash blended cements (BFA-H) than in the slag-containing binders (BSLAG-H), despite the higher intensity of the signals for unreacted clinker in the latter.

Portlandite was not detected in the BFA-C pastes (pastes hydrated in the presence of the alkali) at any of the ages studied, and the sole crystalline phase observed was calcite. By contrast, unreacted clinker, portlandite (albeit in smaller amounts than in the material with no alkalis) and a calcium carboaluminate hydrate, as well as calcite, were identified in both the 2- and 28-day diffractograms for the BSLAG-C pastes. Although no studies were conducted at earlier ages, the formation of this carboaluminate hydrate may very possibly have been associated with the presence of the third peak observed on the heat flow curves for these pastes (see Figure 1(b)).

All the XRD patterns also exhibited halos at 2Θ angles of 25-35°, attributed to the formation of a gel (possibly a calcium aluminosilicate hydrate), the substance to which the mechanical properties of these *hybrid cements* is primarily attributed.

Since scant information on the composition and structure of the gel, which is amorphous to XRD, could be obtained with that technique, further exploration was performed with MAS-NMR. The ^{27}Al and ^{29}Si NMR findings for the starting materials and 28-day binders are shown in Figure 5.

The ^{27}Al and ^{29}Si MAS-NMR spectra for the starting materials, described in earlier papers [6, 12-13], are included here merely to illustrate the profound structural change that took place. The ^{27}Al MAS-NMR spectra for BFA-H and BFA-C exhibited a wide signal at around +57 ppm associated with tetrahedral Al (Al$_T$). A substantial portion of the component of this signal may have been induced by the presence of unreacted fly ash. The higher intensity of the signal, however, along with a slight narrowing and a shift toward higher δ (ppm) values on the spectrum for the BFA-C blend, suggests that much of the Al formed part of a gel in which it was surrounded by four silicon atoms [6, 10,12-13]. The signal observed at around +10 ppm in blend BFA-H, associated with octahedral aluminium (Al$_O$), may be attributed to the calcium aluminate hydrates formed during hydration of the C$_3$A present in the clinker (in the absence of sulphates). 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 other
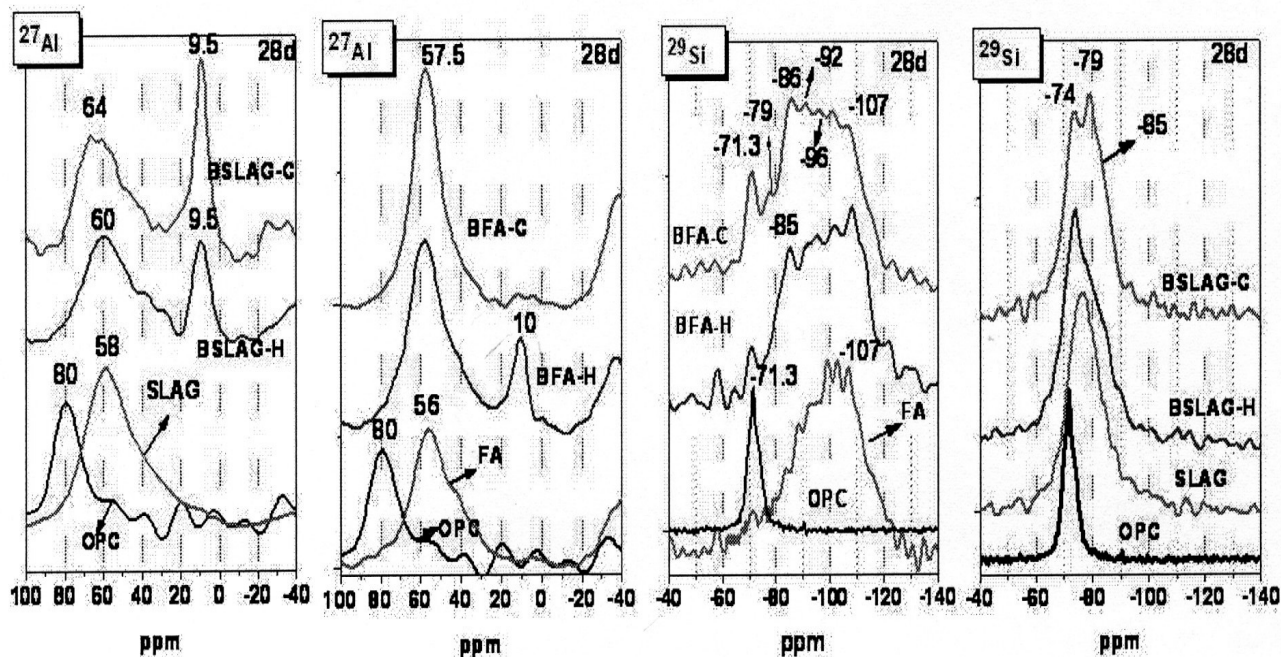
Fig. 5 - ^{27}Al and ^{29}Si MAS-NMR spectra for starting materials and 28-day binders / *Spectrele MAS- RMN cu evidenţierea* [27]*Al şi* [29]*Si, în materialele iniţiale şi în pastele liante la 28 de zile.*

techniques such as XRD.

Both BSLAG spectra exhibited an intense signal at +9.5 ppm associated with Al_O. This signal was much more intense in BSLAG-C, possibly due to the presence of Al in the calcium carboaluminate hydrates also detected by XRD. The AL_T signal appeared at +60 ppm in both cases, indicating that while a considerable amount of Al had yet to react (see slag signal), the aluminium that did react was less polymerised than in the BFA cements [14].

Interpretation of the ^{29}Si MAS-NMR spectra is more complex. The intensity of the signal at -71.3 ppm (associated with the presence of alite + belite in the clinker) was observed to decline in all the hydrated materials, confirming that the calcium silicates in the clinker were reacting.

Two new signals observed in the BFA cements at around -79 ppm and -85 ppm may have been associated with the Q^1 and Q^2 units respectively typical of a C-S-H gel. The high intensity of the component associated with unreacted fly ash in binder BFA-H (no alkaline activator), which revealed the existence of a large amount of unreacted ash, would explain the lower mechanical strength observed for this material. On the BFA-C spectrum, the slight shift of the signal at -85 ppm to -86 ppm and the existence of the signals at -92 and -96 ppm (possibly associated with Q^3(nAL) or Q^4(nAl) units) would be indicative of greater fly ash reactivity in this cement. The inference drawn would be that two types of gel were initially forming in this system: i) a C-S-H gel taking aluminium into its structure as a result of clinker hydration → C-(A)-S-H gel); ii) a N-A-S-H

gel taking Ca into its structure as a result of the alkaline activation of the ash → ((N,C)-A-S-H gel)[9].

The signal at -74 ppm on the ^{29}Si MAS-NMR spectra for the BSLAG cements was strikingly high, perhaps because the signals for the silicates in the clinker and the unreacted slag overlapped. This would corroborate the XRD finding to the effect that the degree of clinker reaction in these pastes was lower than in the BFA materials. A new signal at -79 ppm and a shoulder at -85 ppm were observed in the spectra for both BSLAG-H and BSLAG-C. These signals were again associated with the Q^1 and Q^2 units in a C-S-H gel. The higher intensity of the signal at -79 than at -85 ppm in both spectra suggests the formation of scantly polymerised and similar gels.

The present findings indicate that in the hybrid cements hydrated with water in the absence of activators (BFA-H and BSLAG-H), the clinker (20 % of the material) reacted first, after which the ash or slag reacted with the $Ca(OH)_2$ produced during clinker hydration (pozzolanic reaction). Due to the low clinker and high ash or slag content, this process was observed to be slow, particularly in the case of the fly ash. As a result, the material exhibited a long setting time (Table 2), which would explain the low early age strength values observed for these materials (see Figure 2).

In the presence of the alkaline activator, the pH of the aqueous solution rose, accelerating fly ash or slag dissolution. That led to substantially higher reactivity, shorter setting times and greater early age strength.

Differences were observed in setting time behaviour depending on whether the supplementary material was slag or fly ash.

The presence of alkalis accelerated the initial dissolution of blast furnace slag, releasing (SiO_4 and Ca^{2+} ions into the media, along with smaller amounts of $Al(OH)_4^-$ and Mg^{2+}. That, combined with the SiO_4 and Ca^{2+} ions released during clinker silicate hydration, swiftly saturated the medium, reducing both calcium silicate and slag solubility due to the common ion effect. A second consequence was the accelerated formation and precipitation of C-S-H or C-A-S-H gels [12], which covered both the unreacted clinker and unreacted slag particles. Dissolution was therefore further retarded and ultimately governed by diffusion. That reaction mechanism may explain why binder BSLAG-C exhibited more intense heat release curves and shorter setting times, as well as lower initial (2-day) strength values, than cement BFA-C. Over time, however, the former material continued to react and its mechanical strength grew considerably.

In the fly ash (BFA-C), the heat initially generated by clinker hydration, together with the presence of the alkalis, accelerated the initial dissolution of the vitreous component. In this case, in addition to the SiO_4 and Ca^{2+} ions from the clinker silicates, the medium received SiO_4^- and $Al(OH)_4^-$ ions from the ash. Given the low clinker content (20 %) and the fact that fly ash contains practically no Ca, the medium would hardly become Ca^{2+}-saturated. Several reactions that compete for Ca^{2+} ions may take place in these cements, a circumstance that may accelerate the initial reaction of the calcium silicates in the clinker (see Figure 4(a)) and, indirectly, the initial ash reaction. These possible reactions are: *i*) reaction between Ca^{2+} ions and silicates to form a C-S-H-gel $\rightarrow$ C-(A)-S-H [13]; *ii*) replacement of the Na in the gels formed in the alkaline activation of the fly ash: N-A-S-H $\rightarrow$ (N,C)-A-S-H; *iii*) possible carbonation processes.

These competitive reactions might be the reason why the setting times and peak associated with gel precipitation appeared at slightly later times on the calorimetric curves for cement BFA-C than on the curves for cement BSLAG-C (see Figure 1, Table 2). The latter cement's higher 2-day mechanical strength values (20 MPa, see Figure 2) would be attributed to the larger amount of material that initially reacted (see Figures 4 and 5). The ongoing reaction would lead to a depletion of the source of alkalis over time, however. Consequently, even though mechanical strength continued to rise in the ash-containing binder, that rise was less steep than in cement BSLAG-C because the BFA-C material required more energetic conditions to react.

4. Conclusions

The present findings showed that (*hybrid cement*) binders can be manufactured with a very low (20 %) clinker content and high (80 %) percentages of industrial by-products such as blast furnace slag or fly ash, if the blends are alkali-activated. In the presence of an alkaline activator, these cements exhibit good early age mechanical development, with 2-day values of over 15 MPa, and suitable setting times.

When the cement blend has a high initial calcium content (BSLAG-C), strength development can be attributed primarily to the mix of C-S-H and C-A-S-H gels forming. By contrast, when the Ca content in the blend is lower (BFA-C), the mix formed contains more polymerised C-A-S-H and (N, C)-A-S-H gels.

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