Co-activation of Blended Blast Furnace Slag and Fly Ash with Sodium Sulfate and Hydroxide

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Abstract. The addition of sodium sulfate (Na_2SO_4) to alkali-activated blast furnace slag (BFS), specifically when sodium hydroxide (NaOH) is used as an activator, allows to reduce the amount of hydroxide necessary to achieve desirable mechanical properties. This kind of activation is suitable for BFS that does not require very high pH to promote its hydration. However, it might fall short in case of hybrid binders such as mix of BFS and fly ash (FA). The objective of this study is to elucidate whether the co-activation with Na_2SO_4 and NaOH of these blended mixes leads to advantages compared to just NaOH. The effectiveness of such activation on blended systems is evaluated by means of isothermal calorimetry, products assemblage and compressive strength. The FA replacement significantly affects the induction period length, especially when low NaOH concentration is used, leading to poor early age properties. Nevertheless, the obtained results show that, at later ages, it is still possible to obtain mechanical properties suitable for practical application.

Keywords: Alkali-activated materials · Sodium hydroxide · Sodium sulfate · reaction kinetics · Compressive strength

1 Introduction

Alkali-activated materials (AAMs) provide a promising route in dealing with the environmental impacts of Portland-cement-based building materials. Despite some controversies about the actual carbon emission of alkali-activated binders, it is well accepted that these materials have a significantly lower carbon foot print, compared to Portland cement, due to the different sourcing of the binders that are commonly obtained as industrial by-products [1, 2]. One big disadvantage of these binders is their low or even nil reactivity in water. This drawback is overcome by mixing those binders with high alkaline solutions, made from sodium hydroxide and sodium silicate, leading to materials with high mechanical properties, even superior to those of Portland cement. However, a significant carbon emission is associated to the production of both NaOH and waterglass [3]. A possible alternative to those activators is represented by the near-neutral salts, e.g. carbonates and sulfate [4]. The use of Na_2SO_4, obtained from natural sources (e.g. thernardite and mirabilite) and as industrial by-products, offers unquestionable advantages in terms of environmental impact, cost, ease of use and reduced shrinkage. On the

other hand, sulfate activation often results in a low reactivity of the system, leading to weak mechanical properties [5]. Moreover, the neutral nature of this salt also hinders the possibility to use fly ash (FA) and metakaolin whose activation is strongly pH dependent [6]. These low-calcium materials require pH much higher than 14 to reach acceptable reaction rate. Many studies investigated how to enhance the reactivity of sodium sulfate activated blast furnace slag (BFS) based on BFS composition, fineness and curing temperature [4, 7, 8]. Compressive strength in the order of 45 MPa was obtained from very fine sulfate activated BFS cured at 40 °C while strength of 41 MPa was achieved at room temperature by using wet-grinded BFS with a particle size of 3.87 μm [7]. Another approach to enhance the reactivity of the system consists of providing an initial boost of hydroxyl ions through the addition of limited amount of NaOH, several times lower than what it is generally used [9]. The carbon emissions associated to these systems can be further reduced by partially replacing BFS with FA. A recent study investigated the sodium sulfate activation of ultra-fine BFS (D50 of 3.1 μm) blended with FA [10]. A compressive strength of 60.8 MPa was achieved, at 90 days, with 20% FA and 4% Na_2O, even though in the same a strength of 77.3 MPa was achieved with pure slag. The pH values between 12 and 13 are reported for solutions leached from sulfate activated slag and slag/fly ash [8, 10]. In this pH interval the reactivity of FA is very limited and presumably mainly acts as a filler [11]. In this study the NaOH-Na_2SO_4 approach is followed. The addition of both sodium hydroxide and sulfate shows a synergistic effect on the activation of BFS and leads to appreciable reaction kinetics and mechanical properties. Compressive strength of around 20 and 30 MPa, at 7 and 28 days respectively, was obtained by using 1M $NaOH_{(aq)}$ in combination with Na_2SO_4 while the same BFS activated with higher [NaOH] (e.g. 2M) reached around 17 and 25MPa at the same ages [9]. The presence of a certain concentration of OH^- ions in the activating solution can also promote the hydration of the low reactive FA and be beneficial for the later ages mechanical properties. The aim of this study is to investigated the possibility associated to the activation of blended BFS/FA binders with relatively low alkaline solutions; compared to high alkaline and near-neutral AAMs' compositions these kind of systems might offer a favorable compromise between mechanical properties, low environmental impact, cost and ease of use. The reaction kinetics, products assemblage and the mechanical properties development of different BFS/FA ratios and NaOH concentration are investigated to understand whether or not the hydroxide-sulfate co-activation is able to sufficiently promote the hydration of the binders and lead to materials suitable for practical applications.

2   Materials and Method

The raw materials used in this study are BFS, with a D50 of 9μm, and FA F10, purchased respectively from Ecocem and Bauminerals. Their chemical compositions, retrieved from XRF, are reported in Table 1. While the XRD patterns are reported in Fig. 1. The activating solutions were made by dissolving the appropriate amounts of sodium hydroxide (≥97%) and sodium sulfate anhydrous (≥98%) in distilled water.

BFS and FA were dry mixed in two different ratios: 80% BFS-20% FA and 60% BFS-40% FA. Each blend was activated with three different solutions where the Na_2SO_4

concentration was kept constant at 0.6M while NaOH was added to achieve concentrations of 0.5, 1 and 2M. All the solutions were prepared in advance and let cool down to room temperature (20 °C) before being used. The solution to binder ratio of all the investigated compositions was fixed at 0.5. All the details concerning the mix design are reported in Table 2.

Table 1. Chemical composition of BFS and FA retrieved by XRF

Oxides wt.%	BFS	FA
CaO	40.80	4.33
SiO_2	33.30	56.70
Al_2O_3	12.30	23.50
MgO	7.84	1.43
SO_3	2.30	1.16
TiO_2	1.29	1.23
K_2O	0.67	2.65
Na_2O	0.44	0.91
Fe_2O_3	0.39	5.92
MnO	0.36	–
BaO	0.11	0.21
P_2O_5	–	1.49
SrO	–	0.15

Table 2. Details of the mix design

	BFS %	FA %	Solution/binder	$[Na_2SO_4]$	[NaOH]	Na_2O-E %	Water/binder
A0.5	80	20	0.5	0.6	0.5	2.42	0.45
A1	80	20	0.5	0.6	1	3.22	0.44
A2	80	20	0.5	0.6	2	4.33	0.43
B0.5	60	40	0.5	0.6	0.5	2.42	0.45
B1	60	40	0.5	0.6	1	3.22	0.44
B2	60	40	0.5	0.6	2	4.33	0.43

The hydration kinetics was investigated by means of isothermal calorimetry, up to 72 h, using a TAM Air isothermal calorimeter kept at 20 °C. The signals are normalized by the mass of binder in the measured sample.

The compressive strength was determined on mortar specimens prepared following the standard EN 196-1 with a sand/binder ratio of 3. The mortar was casted in steel molds, wrapped in plastic foils and cured in a room kept at 20 °C and 60% RH. At the
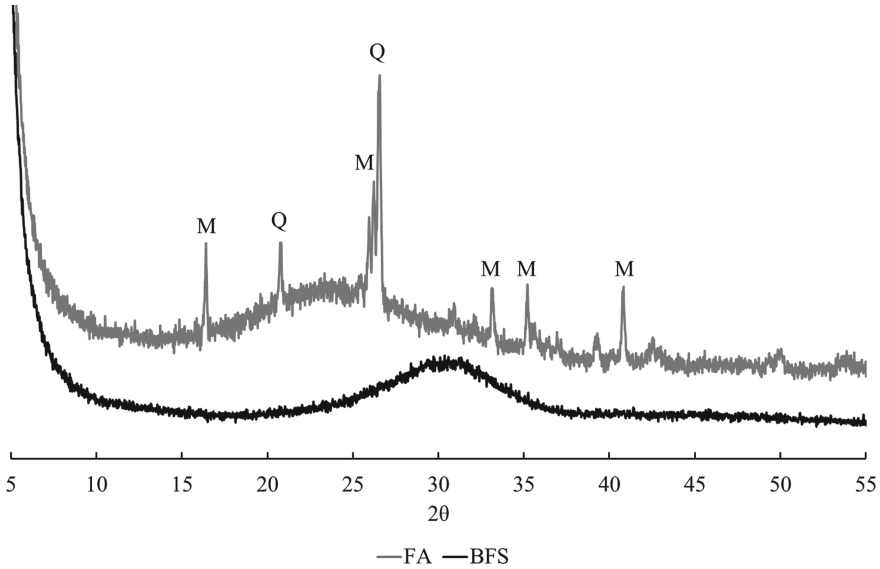
Fig. 1. XRD of the raw materials (Q = Quartz, M = Mullite)

first day of testing the specimens were removed from the molds and cured in a room at 20 °C and ≥85% RH. The compressive strength was tested at 3, 7 and 28 days on pieces of around 40 × 40 mm obtained by splitting the prism into two halves. The composition B0.5 was not tested at 3 days due to its prolonged setting.

The reaction products assemblage was investigated by XRD. A thin slice was cut from paste specimens cured at 20 °C in sealed condition and immediately placed on the sample holder of a Bruker D2 Phaser (Cu Kα radiation). The XRD patterns were recorded from 5 to 55° 2θ with a step width of 0.02 2θ and counting time of 0.3s per step.

3   Results and Discussion

3.1   Reaction Kinetics and Reaction Products Assemblage

The heat flow and total heat curves of the investigated compositions are reported in Fig. 2a, b respectively. It can be noted that the FA replacement has less influence on the reactivity than the concentration of OH^- ions in the activating solution. Nevertheless, the difference between different blends activated with the same solution increases as [NaOH] is reduced. This behavior is expected since it is known that high alkalinity is required to promote FA dissolution and thus its hydration [12]. Due to relatively low [NaOH] investigated in this study, and the short period over which the heat release is evaluated, it is plausible that, in this initial stage, FA mostly behaves as filler. Despite the different intensity there is not a much shift in the hydration peak for samples activated with 2M NaOH, estimated in a couple of hours. If we compare instead A1 and B1, we observe that the time occurring to reach the maximum heat flow in B1 is twice that of

A1. The same comparison cannot be done for A0.5 and B0.5 since the latter does not reach its maximum in the investigated time frame.
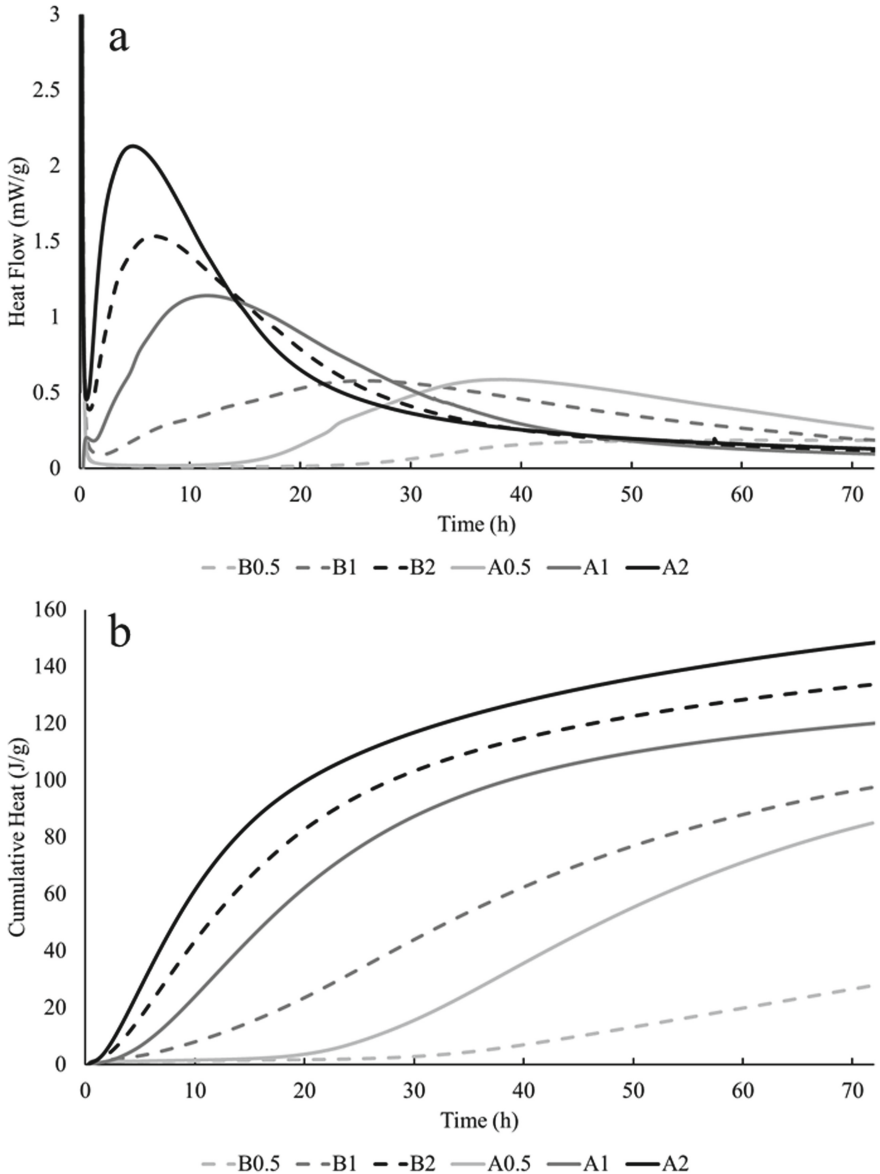

Fig. 2. Heat flow (a) and cumulative heat release (b) evaluated up to 72 h

Among the studied compositions only A0.5 and B0.5 exhibit a proper induction period while the peak's shift of the others is mainly due to the broadening of the peak itself. The cumulative heat release in Fig. 2b confirms the observation made on the heat

flow. After 3 days A2 has the highest total heat, 148 J/g, followed by B2 that reaches 133 J/g. The gap evaluated between compositions with different FA replacement and same activating solution increases to 23 and 57 by reducing [NaOH] to 1 and 0.5M respectively.
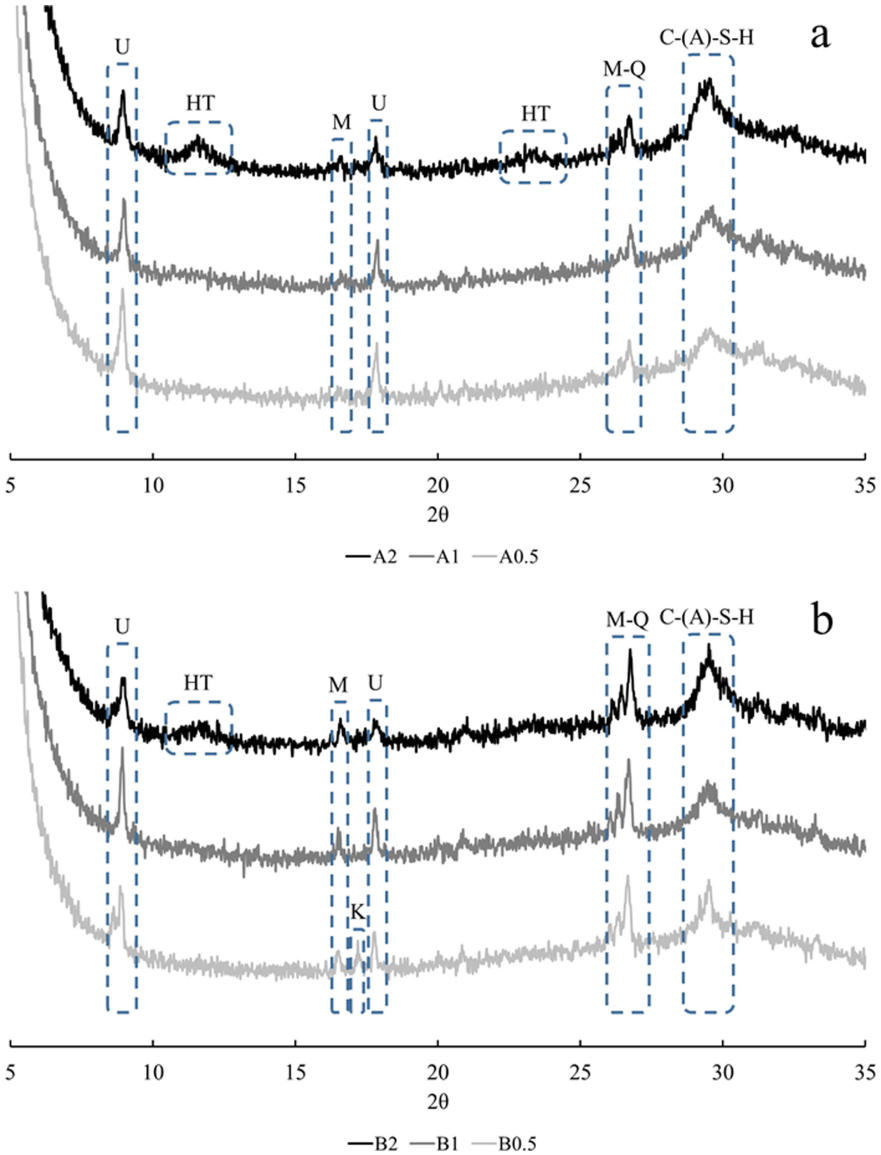

Fig. 3. XRD of A (a) and B (b) series recorded at 7 days without stopping the hydration

The diffraction patterns are reported in Fig. 3a, b for A and B series respectively. The same phases are detected in all the patterns with the exception of hydrotalcite (HT), formed only when 2M NaOH was used in the activating solution, and katoite (K), whose peak is present only in B0.5. The C-(A)-S-H broad peak and two very sharp peaks associated to the U-phase (U), a sodium substituted AFm phase with composition $4CaO.0.9Al_2O_3.1.1SO_3.0.5Na_2O.16H_2O$ [13], are clearly visible in all the patterns. The identified C-(A)-S-H peak, growing on top of BFS' amorphous bump, indicates a partial crystallinity of the product. As reported by many authors, the C-(A)-S-H originated from BFS hydration is characterized by higher crystallinity compared to that from OPC hydration [14–16].The detected mullite (M) and quartz (Q) are due to the presence of FA and the intensity of their peak is proportional to the percentage of FA replacement. Despite the significant amounts of sulfate added through the activating solution, ettringite was not detected and the only sulfate-phase in the investigated compositions is the U-phase. The latter is reported to be stable only at high pH; conditions in which ettringite is unable to precipitate [17, 18].

3.2 Compressive Strength

The results obtained from compressive strength tests are reported in Fig. 4. Each composition was tested at 3, 7, and 28 days except for B0.5 that was still not set at 3 days. At low FA replacement (A series), a substantial difference is present only in the strength developed at 3 days when A0.5 reaches only 3 MPa while A2 has around 19 MPa of compressive strength.
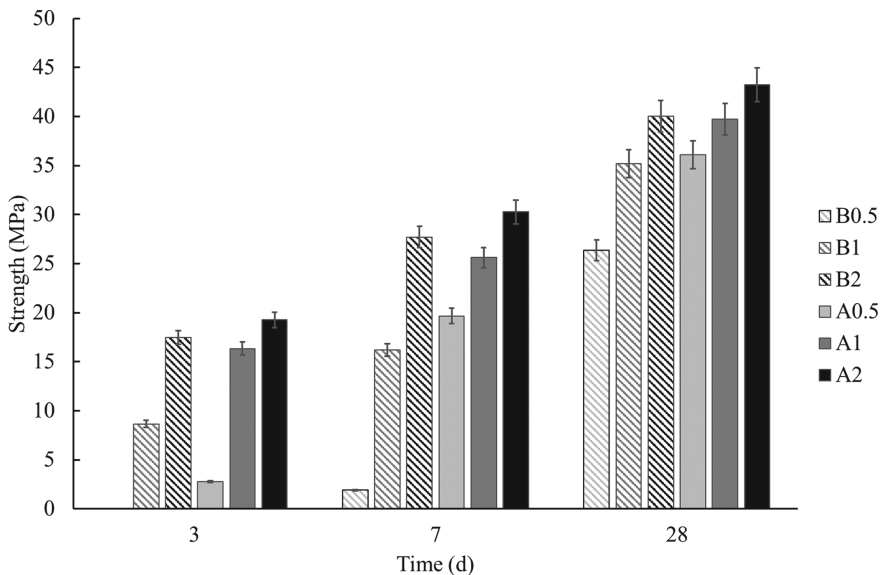

Fig. 4. Compressive strength developed at 3, 7, and 28 days

This difference is substantially reduced at later ages when a contribution from FA is expected. At 28 days A0.5 reaches a notable 36 MPa while A2 reaches 43 MPa. In contrast to the A series, in the B series a significant difference persists between the three compositions also at 28 days, even though this is drastically reduced compared to 3 and 7 days. The 28-day strengths achieved in this study is comparable to those obtained from Zhang et al. [10] on ultra-fine BFS/FA blends activated with sodium sulfate. While they observed a reduction of the mechanical properties due to the incorporation of FA, compared to 100% BFS, the mechanical properties of these blended systems are higher than in pure ones when sulfate and hydroxide solutions are used together. The 28-day compressive strength obtained with 100% BFS and the same activating solution used for B1 and A1(Na_2SO_4 0.6M and NaOH 1M) was significantly lower compared to what is achieved with blended binders within this study [9]. This further corroborates the idea that, in absence of an initial alkalinity boost, the pH reached by the pore solution is not sufficient to promote the reaction of FA even at later ages. In contrast, if a certain [OH^-] is provided, even as low as in A/B0.5 and thus not able to efficiently promote FA reaction within the first days, as shown by calorimetric results, it seems that the alkalinity achieved by the pore solution leads to a FA contribution after prolonged curing.

4   Conclusions

In this study the activation of blended BFS/FA with sodium sulfate and hydroxide was studied in terms of reaction kinetics, products assemblage and compressive strength. Both the isothermal calorimetry and the compressive strength development show that the FA replacement influence on the reaction kinetics and mechanical properties increase as the alkalinity of the activating solution decreases. The reported results show that it is possible to efficiently activate BFS/FA blended binders with a combination of sodium sulfate and hydroxide even when solutions with a low sodium content (i.e. 2.42%) are used. The addition of FA induces a significant increase in the induction period and subsequent delay in the mechanical properties development. However, a minimum of around 25 MPa can still be achieved at 28 days at high FA percentage (40%) and with a limited addition of NaOH (0.5M). It seems that a certain OH^- concentration should be initially provided through the activating solution, even without exceeding a pH of 14, to observe contributions due to the hydration of FA thus it might not be possible to properly activate blended AAMs by using only near-neutral activators such as sodium sulfate.

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