Hybrid Alkaline Cements: Bentonite-Opc Binders

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Abstract: Moderately alkaline activators can be used to formulate cementitious binders with a high Supplementary Cementitious Materials (SCMs) and a low portland cement content (hybrid alkaline cements). This study aimed to prepare hybrid alkaline cements containing large percentages of dehydroxylated bentonite (BT) and small Portland cement (OPC) fractions, with 5% Na₂SO₄ as a solid alkaline activator. The hydration kinetics of the pastes hydrated in water in the presence and absence of the solid activator were assessed by isothermal conduction calorimetry, whilst the reaction products were characterised with X-Ray Powder Diffraction (XRD) and Fourier-transform Infrared Spectroscopy (FTIR). The presence of the alkaline activator hastened OPC and BT/OPC hydration: more heat of hydration was released, favouring greater initial bentonite reactivity. The portlandite forming during cement hydration reacted readily with the Na₂SO₄, raising medium alkalinity and enhancing bentonite dissolution and with it reaction product precipitation (primarily (N,C)-A-S-H-like gels that co-exist with C-S-H- or C-A-S-H-like gels). The presence of sulfate ions favoured the formation of AFm-like phases. Preceding aspects accelerated the hydration reactions, with the formation of more reaction product and matrix densification. As a result, the 28 days Na₂SO₄ activated systems developed greater mechanical strength than the water-hydrated systems, with the 60% BT/40% OPC blends exhibiting higher compressive strength than the 100% OPC pastes.

Keywords: alkaline activation; geopolymer; hybrid cements; calorimetry; bentonites

1. Introduction

The addition of clays as natural pozzolans is standard practice in cement and concrete manufacture [1–3]. The partial substitution of clays for cement purposes primarily to lower production costs by replacing a material (clinker) characterised by an energy-intensive manufacturing process. This practice also reduces the industry’s environmental footprint by lowering CO₂ and other greenhouse gas emissions and affords certain technological benefits. The use of mineral additions (pozzolans) in concrete reduces porosity, raises resistance to aggressive agents, lowers heat of hydration and thermal expansion and enhances fresh mix workability. Whilst initial strength may sometimes decline, the later age values may be higher than in OPC [4].

To be viable cement additions, most clays must be activated by grinding and burning [1–3]. Calcination dehydroxylates and induces structural collapse in clay, converting it into a more disorderly and reactive material. Kaolinite (metakaolinite after calcination) clays are the ones most commonly used for these purposes, for as a rule they improve workability, durability and strength [1–3]. Their use entails certain drawbacks, however: the high purity required is often difficult to obtain and the extraction, purification and calcination involved in obtaining the end product, metakaolin, carry a high energy price tag.

Another important factor to bear in mind when preparing SCM-containing mortars and concretes is the maximum amount of pozzolan (burnt clay in this case) that can be added. That ceiling is limited
(normally to 11% to 35%) by the legislation in effect, for whilst in certain proportions its effects are beneficial, very high replacement ratios may deliver the opposite result [1–3]. The formulation of “portland–alkaline” hybrid cements is an innovative way to raise clay content in cement without adversely affecting its mechanical properties. Portland-alkaline hybrid cements are multi-component systems containing a large fraction of mineral additions and a small proportion of portland cement [5–7]. In the presence of alkaline activators, these systems set and harden into materials with excellent cementitious properties, comparable to or better than those of traditional portland cement [5–7]. The hybrid binders most commonly studied contain blends of portland cement or clinker and blast furnace slag, coal fly ash or both [5–9]. Whilst the use of the aforementioned additions delivers environmental benefits and lowers costs, these materials may pose problems of availability and uniformity, largely solvable if clay is used in their place.

In addition to broadening the range of “alkali-activatable” materials, preparing hybrid cements with clay would lower the industry’s environmental impact by using abundant mineral resources in lieu of the limestone and others normally quarried to manufacture cement. Calcination substantially enhances the viability of the use of clay and feldspar in alkaline activation [10]. Dehydroxylation in the 550 °C to 850 °C range eliminates OH− groups, with a considerable rise in clay reactivity and the formation of highly amorphous silica- and alumina-based materials (xSiO2·yAl2O3·zH2O→(SiO2)x·(Al2O3)y+zH2O) potentially usable as raw materials in alkaline cement manufacture [11,12].

A number of papers have been published on the use of dehydroxylated clays (alone or in combination with other materials) as raw materials in the manufacture of new alkaline cementitious binders [11–13]. Most of those studies focused on kaolinite clays (primarily metakaolinite), with very few exploring other materials such as bentonite [14,15]. Prior research published by the authors showed that the latter clay is apt for use in alkaline hybrid cements [15].

Conventional alkaline cements (or hybrid alkaline cements) prepared with alkaline solutions have some inconveniences [16]. The hazards involved in handling the corrosive solutions normally used (which contain soluble silicates or hydroxides) have driven the scientific community to seek solid activators able to deliver ready-mix cements. In these ready-mix cements (also called “one-part alkaline activated cements” [16]), only a dry mixture is needed in addition to water. The dry mixture is prepared by mixing the precursor, in this case the OPC + the dehydroxylated bentonite, with the solid activator.

This study explored two key factors that contribute to the cementitious properties of such binders: (i) the hydration kinetics of the new cementitious systems in which the clay used is a dehydroxylated bentonite; and (ii) the type of reaction product generated (cementitious gel) in the presence of a solid activator (moderately alkaline salts) such as Na2SO4.

2. Experimental

2.1. Materials

A type I 52.5 R portland cement (OPC) and Algerian bentonite (BT) were used in this study. The bentonite was thermally activated (dehydroxylated) at 750 °C for 5 h (BT). Starting material chemical and mineralogical compositions are given in Table 1.

<table>
<thead>
<tr>
<th>Raw Material</th>
<th>Chemical Composition (XRF, wt %)</th>
<th>Mineralogical Composition (XRD)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LoI (2) SiO2 Al2O3 CaO Na2O K2O Fe2O3 MgO SO3 Other</td>
<td>Albite (alb: NaAlSi3O8); Quartz (q: SiO2) (amorphous phase (3) 66.58%)</td>
</tr>
<tr>
<td>BT (3)</td>
<td>0.56 62.6 17.93 1.60 6.56 2.37 3.12 3.89 0.87 0.83</td>
<td>(C3S); Belite (C2S); Ferritic phase (C4AF); Tricalcium aluminate (C3A); gypsum (g: CaSO4·2H2O)</td>
</tr>
<tr>
<td>OPC</td>
<td>2.56 20.26 6.33 62.70 0.59 0.79 2.30 0.18 2.82 1.47</td>
<td></td>
</tr>
</tbody>
</table>

BT = dehydroxylated bentonite (750 °C, 5 h) with 95% of particles <45 μm and 82% <30 μm; (2) loss on ignition at 1000 °C; (3) determined by 1% HF attack.
The alkaline activator used was 99.99% pure commercial solid sodium sulfate (Na$_2$SO$_4$), supplied by PANREAC.

2.2. Methods

The cementitious binders consisted in blends of different proportions of portland cement (OPC) and dehydroxylated bentonite (BT): B1 (80% BT/20% OPC), B2 (70% BT/30% OPC) and B3 (60% BT/40% OPC). Half of the blends, labelled “NS”, were additioned with 5% (relative to the total weight of the blend) solid Na$_2$SO$_4$ as an alkaline activator. The other half, labelled “H”, was prepared without the alkaline activator. The control samples consisted in 100% portland cement (labelled “100% OPC”) and 100% dehydroxylated bentonite (labelled “100% BT”).

The early age hydration kinetics in the cement/bentonite blends were analysed via isothermal conduction calorimetry on a THERMOMETRIC TAM Air analyser (TA instruments, Wetzlar, Germany) at a constant 25 °C. The heat released by water was used to establish the calibration base line. Test samples were prepared with 5 g of solid at a water/binder ratio of 0.4 and mixed for 3 min prior to placement in the calorimeter, from which they were removed 120 h (5 days) after initial mixing.

Prismatic paste specimens (1 × 1 × 6 cm$^3$) were prepared with the bentonite-cement blends, also at a constant water/binder ratio of 0.4, and cured in a climatic chamber at 22 ± 2 °C and RH = 99% until the 2 days or 28 days test age. Twelve specimens were tested for mechanical strength at each age on an Ibertest Autotest-200/10-SW test frame.

The pastes were characterised by XRD (at the test ages on a BRUKER AXS D8 ADVANCE diffractometer (BRUKER, Billerica, MA, USA) fitted with a high voltage, 4 kW Cu X-ray tube, operating at 40 kV and 50 mA. FTIR spectra, likewise recorded at the test ages, were recorded from specimens containing 1 mg of sample mixed with 300 mg of KBr on an ATI Mattson FTIR-TM spectrometer (Triad Scientific, Manasquan, NJ, USA) operating at a resolution of 4 cm$^{-1}$ in the 4000 cm$^{-1}$ to 400 cm$^{-1}$ range.

3. Results and Discussion

3.1. Calorimetric Study

The heat flow (in J/g·h) and total heat release (J/g) curves for both the Na$_2$SO$_4$-activated and water-hydrated cementitious binders are reproduced in Figures 1 and 2. The most representative findings are discussed below.
Figure 1. Heat Flow evolution (J/g·h) of hydrated and alkali activated hybrid cements (a) BT (100% BT); (b) OPC (100% OPC); (c) B1 (80% BT + 20% OPC); (d) B2 (70% BT + 30% OPC) and (e) B3 (60% BT + 40% OPC).

Figure 2. Cont.
Figure 2. Total Heat (J/g) of hydrated and alkali activated hybrid cements (a) BT (100% BT); (b) OPC (100% OPC); (c) B1 (80% BT + 20% OPC); (d) B2 (70% BT + 30% OPC) and (e) B3 (60% BT + 40% OPC).

3.1.1. 100% OPC (OPC)

The calorimetric curve for the 100% OPC hydrated exclusively with water (OPC-H) was typical of portland cement hydration calorimetric curves (Figure 1b) [17,18]. The peak denoting clinker phase dissolution and the possible precipitation of primary ettringite was practically undetectable, inasmuch as those reactions took place very rapidly and part of the information was inevitably lost during mixing prior to placement in the calorimeter. The peak with a maximum at around 7.3 h (Figure 1b), characteristic of portland cement hydration, was associated with the mass precipitation of C-S-H gel + Ca(OH)$_2$ [17]. The shoulder appearing at around 10 h was attributed to AFt phase precipitation [17].

The heat flow curve for the same binder hydrated in the presence of the alkaline activator (OPC-NS, Figure 2b) was similar to the curve for the water-hydrated system, although in this case the presence of alkalis (Na$^+$) and SO$_4^{2-}$ ions in the medium shortened the induction period slightly, hastening precipitation of the main reaction products (the peak was brought forward by around 1 h, to 6.27 h (see Figure 1b). Further to the literature, the presence of alkaline sulfates accelerates OPC hydration and delivers high early age strength [19].

The presence of the alkaline activator however seems not affects the total heat released. After 120 h the total heat released by OPC-NS is slightly higher than the non-activated sample (OPC-H, see Figures 2b and 3).
Figure 3. Total Heat (J/g) for the different systems after 120 h of hydration.

3.1.2. 100% BT (BT)

The binder consisting in 100% water-hydrated bentonite (BT-H) exhibited no heat exchange (Figures 1a and 2a). Dehydroxylated bentonite, water hydrated in the absence of alkalis at ambient temperature, behaved like a practically inert material lacking hydraulic properties. Much the same behaviour was observed in the presence of the alkaline activator (BT-NS: see Figures 1a and 2a). At ambient temperature and moderate alkalinity, bentonite neither set nor hardened.

The low intensity peak appearing in both BT-H and BT-NS in the first few minutes of hydration (Figure 1a) was generated in all likelihood by the partial dissolution of one of its chemical constituents.

3.1.3. Hybrids (B1, B2 and B3)

When water-hydrated, all the binders bearing different proportions of bentonite and portland cement generated heat flow and total heat curves very similar to the curves observed for the reference portland cement (OPC-H; see Figure 1b). Certain differences were nonetheless detected. The peak associated with reaction product precipitation shifted to slightly shorter hydration times, while the total heat released (Figure 2c–e) was on the order of two to three times lower than in the 100% OPC. Total heat released was proportional to and rose with the amount of cement used in the blend (see Figure 3). Those findings can be explained by the dilution effect: the amount of cement available in the binder was considerably lower than in the reference OPC-H (100% OPC). The dilution factor alone, however, would have lowered the total heat in binders B1-H, B2-H and B3-H even further. For instance, the heat of hydration generated by the cement alone in B1-H would have yielded total heat of 68 J/g instead of the 123 J/g actually recorded. The difference can be attributed to bentonite pozzolanicity: burnt bentonite reacted with the portlandite, generating more C-S-H gel and contributing to total heat.

The heat flow curves for the activated binders (NS), in contrast, differed significantly from the systems hydrated exclusively with water (H) (Figure 1c–e). In all cases, as observed in the OPC (100% OPC), the presence of the alkaline activator induced much more intense signals, which shifted to slightly shorter times, again suggesting accelerated reaction product precipitation. That the activated systems released more total heat than the respective water-hydrated binders was an indication that the combination of the two raw materials (cement and bentonite) with the activator favoured bentonite reactivity.

3.2. Characterisation of the Reaction Products

The reaction products were characterised by XRD and FTIR to establish the effect of the alkaline activator and the role of bentonite in hybrid cement development. The major crystalline phases detected in each binder by XRD are listed in Table 2.
As in the raw material, quartz and albite were identified in the 2 days and 28 days BT reference (100% BT), although the binders prepared with the alkaline activator also contained calcium sulfate. In addition, calcite was detected in the 28 days water-hydrated binder (Table 2). The interaction of the $SO_4^{2-}$ ions present in the alkaline activator with the scant amount of calcium dissolving out of the dehydroxylated bentonite confirmed some degree of reactivity.

In addition to unreacted clinker particles (alite and belite), the OPC binders contained typical secondary hydration products, primarily portlandite and ettringite, the latter in more significant quantities in the samples containing the alkaline activator. The intensity of the lines for the clinker phases was lower in the alkali-activated binders, where the high calcium content in the system). Higher pH values also accelerated the pozzolanic reaction.

Table 2. XRD-detected crystalline phases.

<table>
<thead>
<tr>
<th>System</th>
<th>Crystalline Phases Detected in the Precursors *</th>
<th>Reaction Products *</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H (Water Hydrated)</td>
<td>NS (Activated)</td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>2 days</td>
<td>OPC</td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td>BT</td>
<td>x</td>
</tr>
<tr>
<td></td>
<td>B1</td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td>B2</td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td>B3</td>
<td>✓</td>
</tr>
<tr>
<td>28 days</td>
<td>OPC</td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td>BT</td>
<td>x</td>
</tr>
<tr>
<td></td>
<td>B1</td>
<td>x</td>
</tr>
<tr>
<td></td>
<td>B2</td>
<td>x</td>
</tr>
<tr>
<td></td>
<td>B3</td>
<td>x</td>
</tr>
</tbody>
</table>

*Nomenclature: A: C₃S (alite); B: C₂S (belite); q: quartz (SiO₂); alb: albite (NaAlSi₃O₈); c: calcite (CaCO₃); g: gypsum (CaSO₄·2H₂O); p: Ca(OH)₂ (portlandite); e: Ca₆Al₂(SO₄)₃(OH)₁₂·26H₂O (ettringite). Key: ✓—present; x—absence.

In all the 28 days BT plus OPC systems, the intensity of the portlandite lines declined substantially, even disappearing altogether in the binders bearing the alkaline activator (NS, see Table 2). Those findings were associated with the combined effect of several factors: (a) BT pozzolanic reaction-mediated portlandite consumption (Equation (1)); (b) atmospheric CO₂-driven carbonation and CaCO₃ formation (Equation (2)); (c) the portlandite-sodium sulfate reaction and greater consumption of portlandite in the presence of the activator (Equation (3)). The third reaction raised the solution pH, which in turn hastened dehydroxylated bentonite dissolution, favouring its alkaline activation and the formation of N-A-S-H-like gels [14] (or (N,C)-A-S-H-like [20] gels as a result of the high calcium content in the system). Higher pH values also accelerated the pozzolanic reaction. The inclusion of Na₂SO₄ raised SO₄²⁻ concentration, inducing the formation of more ettringite (AFT, Equation (4)). According to the literature, AFT phase formation increased the solid volume by 164% (C-S-H gel grows the solid volume by only 17.5% [19,21–23]). AFT densified the structure and raised initial cement paste strength and hardening very significantly, as discussed below.

\[
\text{Ca(OH)}_2 + \text{SiO}_2 (\text{BT}) + \text{H}_2\text{O} \rightarrow \text{C-S-H gel} \quad (1)
\]

\[
\text{Ca(OH)}_2 + \text{CO}_3^{2-} \rightarrow \text{CaCO}_3 + 2\text{OH}^- \quad (2)
\]
\begin{align*}
\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} + \text{Ca} (\text{OH})_2 & \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 2\text{NaOH} + 8\text{H}_2\text{O} \quad (3) \\
\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{C}_3\text{A} + \text{Al}(\text{OH})_4^- & + \text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O} \quad (4)
\end{align*}

(OPC) (BT)

Since the main hydration or activation products (C-S-H, N-A-S-H, C-A-S-H or (N,C)-A-S-H gels) are X-ray-amorphous, their presence had to be identified with other characterisation techniques, specifically FTIR.

The FTIR spectra for the binders hydrated exclusively with water are reproduced in Figure 4 and those for the alkali-activated binders in Figure 5. The figures include the FTIR spectrum for unhydrated/non-activated BT.

The FTIR spectrum for the dehydroxylated bentonite (BT, Figure 4) contained a wide asymmetric band (generated by dehydroxylation) centred at around 1032 cm\(^{-1}\), attributed to the asymmetric stretching vibrations generated by T–O bonds (T = Si or Al) \[23,24\]. The shoulder at 1102 cm\(^{-1}\) was associated with the Si–O bond asymmetric stretching vibrations in amorphous silica \[24,25\]. The main quartz band (phase identified by XRD), normally located at around 1080 cm\(^{-1}\), overlapped with the main band. All the other quartz vibration bands were detected, however: the double band at 796 cm\(^{-1}\) and 775 cm\(^{-1}\) and the band at 697 cm\(^{-1}\), attributed to symmetric Si–O bond stretching vibrations \[26\]. The bands located at around 540 cm\(^{-1}\) and 463 cm\(^{-1}\) were respectively associated with Si–O–Al and Si–O–Si bond bending vibrations \[24,25\].

The spectrum for hydrated BT (BT-H) differed scantly from the spectrum for the anhydrous bentonite (BT), as expected in light of the XRD and isothermal conduction calorimetric findings.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{FTIR Spectra for hydrated systems BT, OPC, B1, B2 and B2 (2 days) from 2000 cm\(^{-1}\) to 400 cm\(^{-1}\) without activator (H-systems).}
\end{figure}
The spectrum for the hydrated cement (OPC-H) exhibited vibration bands associated with C-S-H gel formation: the main band at 980 cm\(^{-1}\), generated by Si–O bond asymmetric stretching vibrations; the band at 668 cm\(^{-1}\), associated with Si–O–Si bond bending vibrations; and the band at 460 cm\(^{-1}\), attributed to Si–O bond bending vibrations in Si\((\text{SiO}_4)\) tetrahedra. The signal at 1630 cm\(^{-1}\) was attributed to H–O–H bond bending vibrations in water [26,27]. Carbonates such as calcite were also identified, with bands at 1428 cm\(^{-1}\), 876 cm\(^{-1}\) and 715 cm\(^{-1}\) related to the various C–O (CO\(_3^{2-}\)) bond vibration modes. The signal at 1126 cm\(^{-1}\) was attributed to S–O bond asymmetric stretching vibrations (normally associated with the SO\(_4^{2-}\) groups in ettringite) [26]. The signal at 520 cm\(^{-1}\) was generated by Si–O bond bending vibrations in unreacted clinker phases (primarily C\(_3\)S) [28], also detected by XRD (Table 2).

The spectra for the hybrid cements hydrated exclusively with water (B1-H, B2-H and B3-H) differed from the preceding, particularly as regards the main band associated with T–O (T = Al or Si) bond vibrations. The spectrum for B1-H (80% BT/20% OPC, Figure 4a) contained a wide asymmetric band centred at 1028 cm\(^{-1}\), which shifted to slightly lower frequencies with rising cement content (Figure 4). The interpretation of this signal is not straightforward, for it was very likely the result of overlapping of a number of types of vibrations, essentially the T–O bond vibration in bentonite and the Si–O bond vibrations in the C-S-H gel (the hydration product of the cement in this blend). The band located at 648 cm\(^{-1}\), together with the signal at 460 cm\(^{-1}\), might confirm C-S-H gel precipitation.

The spectra for the activated (NS) systems (Figure 5) differed from the ones for their water-hydrated counterparts. The spectrum for alkali-activated dehydroxylated bentonite (BT-NS) contained a very wide, asymmetric band peaking at around 1120 cm\(^{-1}\) (\(\nu_{\text{as}}\) S–O SO\(_4^{2-}\)) and a second band at around 1030 cm\(^{-1}\), associated with T-O bond vibrations in bentonite [24]. It also exhibited a signal at 618 cm\(^{-1}\) attributed to sulfate bond bending vibrations that appeared in neither the anhydrous nor the water-hydrated sample [29,30].

The spectrum for the alkali-activated cement (OPC-NS, Figure 5) was practically identical to the spectrum for the water-hydrated material (Figure 4). The sole difference worthy of note was the presence of a narrow, intense signal at 618 cm\(^{-1}\), typical of sulfate bond bending vibrations [29,30],
possibly indicating that not all the sodium sulfate had been consumed at the age studied (either via reaction with the portlandite generated or AFt-like phase formation). Given the position of the band, however, its association with traces of gypsum present in the original anhydrous cement cannot be ruled out.

The spectra for hybrid alkaline cements B1-NS, B2-NS and B3-NS (Figure 5) differed from those for the same binders hydrated in the absence of the activator:

(i) At higher portland cement contents, the main band associated with T–O bond vibrations (B1-NS, 1020 cm$^{-1}$; B2-NS, 1010 cm$^{-1}$ and B3-NS, 999 cm$^{-1}$) shifted toward lower frequencies, narrowed and sharpened. As noted above, this main band overlapped with several others. In this case and given its position, it may have been the result of the overlap between a C-S-H-like gel (cement hydration product) and a N-A-S-H-like gel (product of bentonite alkali-activation).

(ii) The band associated with S–O bond asymmetric stretching vibrations (at around 1110 cm$^{-1}$), more visible and intense in the Na$_2$SO$_4$-activated systems, was associated with the formation of more ettringite in these systems, as previously detected by XRD.

The 2 days and 28 days compressive strength values for the pastes are shown in Figure 6. As the systems comprising 100% dehydroxylated bentonite (BT) failed to harden even in the presence of the alkaline activator, they are not shown on the figure. Both the water-hydrated and alkali-activated 100% OPC (OPC) had strength values on the order of 25 MPa, although the alkaline activator (NS) raised both the 2 days and the 28 days values slightly. The bibliography on the effect of alkaline sulfates on the OPC hydration is contradictory [19,31–33]. While some authors point that the alkali sulfates, in general, accelerate the rate of hydration and give high early strengths [31,33], others indicated that the alkali sulfate additions to cement did not cause changes in the degree of hydration of C$_3$A or C$_3$S components but the strengths can be significantly reduced [33]. In our case we observe both, an acceleration in the hydration reaction (Figure 1b) and a slightly increase in the mechanical strengths (See Figure 6). The acceleration in the hydration yielded a larger amount of reaction product and this could be reflected in the mechanical strength values (Figure 6). However further studies are necessary to clarify this point.

Figure 6. The 2 days and 28 days compressive strength (MPa): B1, (80% BT/20% OPC; B2, 70% BT/30% OPC; and B3, 60% BT/40% OPC.

The effect of the activator was much more perceptible when the binder contained bentonite: blend B3-NS (60% BT/40% OPC), at 53 MPa, exhibited higher 28 days strength than OPC. In all cases and ages (most notably at 28 days), greater strength developed in the presence of the alkaline activator than in its absence, providing clear evidence that bentonite contributed largely to material strength.

Dehydroxylated bentonite played a dual role in alkaline hybrid cement development. In the OPC-BT blended cements without the alkaline activator it participated only in a pozzolanic reaction with the portlandite forming during portland cement hydration, producing more C-S-H gel (Equation (1)) [34] and therefore more reaction product.
In contrast, as mentioned earlier, in the presence of the alkaline activator, the portlandite reacted with sulfates, generating “in situ alkalinity” (see Equation (1)), which would favour the partial dissolution of BT, enhancing the solubility of its silica and alumina and driving N-A-S-H-like gel precipitation. Unlike system BT, none of the blended alkaline binders was observed to contain gypsum (Equation (3)), for it would have reacted very rapidly to form ettringite with the C₃A present in the OPC or with the alumina in the BT, or both (Equation (4)) [20]. That was confirmed by the XRD findings, as noted earlier: the ettringite signals were more intense in the Na₂SO₄-activated systems.

The presence of sodium sulfate therefore induced several complementary effects: it generated alkalinity in the medium, hastening the dissolution of the silica and alumina in the Bentonite, which favoured N-A-S-H-like gel precipitation [14,15,21]; it also enhanced the pozzolanic reaction and the formation of more AFT. All those effects raised the degree of reaction, densifying the material and increasing strength. Similar behaviour has been observed in hybrid alkaline cements containing blends of cement and fly ash [35].

4. Conclusions

In hybrid alkaline cements, the Ca(OH)₂ resulting from cement hydration reacts with Na₂SO₄, generating more alkalis in the system. A higher alkaline content raises the pore solution pH, favouring Bentonite dissolution and the possible precipitation of the products of the alkaline reaction ((N,C)-A-S-H-like gels that co-exist with C-S-H-like gels). The initial heat of OPC hydration also favours the initial Bentonite reaction. Finally, the presence of sulphate ions from the activator also enhances the precipitation of AFT-like phases that densify the matrix and raise system mechanical strength.

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Conflicts of Interest: The authors declare no conflict of interest.

References


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