Study of the fire and thermal behaviour of façade panels made of natural fibre-reinforced cement-based composites

L. Gonzalez-Lopez, J. Claramunt, L. Haurie, H. Ventura, M. Ardanuy

Abstract

The thermal and fire behaviour of calcium aluminates cement-based composites with a variable metakaolin content (from 0 to 40 wt% addition) reinforced with nonwoven flax fabrics has been examined. The fire behaviour was assessed using epiradiator and small-scale fire testing. The composites did not emit smoke or generate flames, nor did they produce spalling. Their integrity was maintained above 1000 °C. Samples having a higher metakaolin content revealed a delay in the temperature of the unexposed surface until reaching 760 °C. The effect of exposure to high temperatures (250 °C, 450 °C, and 950 °C) on bending behaviour was examined. The fibres were found to maintain their reinforcing capacity up to 250 °C, while the matrix maintained its performance up to 450 °C. The addition of metakaolin reduced conductivity and diffusivity. The results of the thermal and fire behaviour of the tested composites indicated that they may be suitable for façade panels for outdoor applications.

1. Introduction

Ventilated façades are constructive systems that form a ventilated air chamber placed between the external cladding and the inner wall of buildings, thereby minimizing thermal bridges and permitting natural ventilation to offer good thermal efficiency. This is the biggest advantage of ventilated façades, which are especially important in warm countries with strong solar radiation. Nonetheless, in the event of a fire, the chimney effect of the air chamber will contribute to the fire’s spread [1]. The fires of the Lincoln City Hotel in Grozny, taking place in April 2013, those of Grenfell Tower, in June 2017, and of Dubai’s Torch Tower, in August 2017 [2–4], are examples of what can happen to a building when appropriate measures are not taken to prevent the spread of fire across the external panels in ventilated façade systems. In all of these examples, the fire that spread through the façade was extremely fast-moving and devastating, generating very intense flames due to the ignition of the façade’s inner and outer materials. Clearly, these ventilated façades should be designed to prevent the spread of fire. Therefore, in addition to fire barriers on the inner elements, the use of fireproof materials on the façade panels can considerably improve a building’s fire behaviour.

Previous studies have shown that nonwoven, vegetable fibre fabrics in reinforced cement composites serve as sustainable materials for applications in façade panels [5–10]. The composites developed are lightweight, have a strain-hardening behaviour, and offer high performance, mainly under bending deformations. Although Portland cement and calcium aluminates (CAC)-based cements with high mechanical performance were developed, an evaluation of their durability to wet dry accelerated aging demonstrated that binary blended CAC-metakaolin (MK)/natural fibre composites were the most suitable for outdoor applications. The microstructure, mechanical performance and durability of these systems have been analysed in detail [9]. No studies, however, have assessed the thermal and fire behaviour of these composites.

Commercial aluminates cement is obtained by melting ferruginous bauxite and calcite at approximately 1450 °C-1600 °C. The chemical composition of the obtained clinker is mostly formed of calcium, aluminium, and iron oxides. Monocalcium aluminates (CA) is the most common phase. In the hydration process, distinct compounds are formed depending on the curing temperature. The CAC is subjected to a process of conversion of the distinct metastable phases that can be formed in the stable phase, so the hydrated cement contains crystalline phases of C2AH8 (hydrogarnet) and amorphous gel or crystalline phases of AH6, depending on the temperature [11].
As for the thermal decomposition of cement, as the temperature increases, certain changes occur in the cement pastes, mainly due to the loss of water either by evaporation of the interstitial water or by transformation of hydrated phases in anhydrous phases. For CAC, the thermal decomposition involves four main steps: a) the evaporation of interstitial water (50 °C-100 °C); b) the dehydration of aluminium hydroxide gel, of \( \text{CAH}_10 \) and \( \text{CAH}_8 \) phases (80 °C-200 °C); c) the transformation of the \( \text{AH}_3 \) crystalline polymorphic phases into aluminium oxide (200 °C-350 °C); and d) the transformation of \( \text{C}_2\text{AH}_8 \) in various phases (350 °C-500 °C) [12,13] until the sintering and formation of \( \text{CA} \), at approximately 1080 °C [14,15]. The resulting oxides are thermally stable, but CAC loses strength due to shrinkage at 400 °C, with an increased porosity of up to 48%. This results in a decreased compression strength by over 20%. The CAC melting point depends on the \( \text{Al}_2\text{O}_3/\text{CaO} \) molar ratio, which is over for higher ratios [16]. The incorporation of different aggregates increases the melting temperature. Aggregates with a high aluminium oxide content are preferred [11]. Regarding the thermal behaviour of MK, temperatures above the dehydroxylation (850 °C) lead to a recrystallisation of the amorphous zones, making it lose its pozzolanic capacity [17,18]. On the other hand, the addition of pozzolanic aggregates to CAC, such as silica fume or fly ash, has been studied as a strategy to mitigate the adverse mechanical effects of \( \text{CAH}_2 \) conversion into stable phases [19-22]. The incorporation of reactive silica produces strätlingite (\( \text{C}_2\text{ASH}_8 \)) to the detriment of \( \text{C}_2\text{AH}_8 \). This phase is stable at the curing temperature range of 20 °C to 70 °C. The strätlingite loses the inter-laminar water at a temperature around 175 °C and the internal water around 210 °C [23].

As for the vegetable fibres, particularly flax fibres, they consist mainly of cellulose (over 60%), hemicellulose (between 2 and 6%), and lignin (between 1 and 6%) [24]. The degradation of the cellulose and hemicellulose occurs around 250 °C-400 °C (with a weight loss of over 75%) [25-27], whereas the lignin decomposes around 200 °C-500 °C [28].

In addition to the residual resistance of the material as a function of the decomposition of its components, another important aspect is the “spalling” effect. The spalling effect is a degradation of the surface of the material that is expelled abruptly or explosively as a result of high internal pressure. This complex effect is mainly caused by migration, through the evaporation and condensation of the free internal water of cements exposed to fire. When this migration causes the saturation of the porous microstructure to limit the escape routes for the water vapour, the internal pressure increases, causing the explosive spalling which results in material flaking off of the surface [28]. This phenomenon is produced in both Portland-type cements [29] and calcium aluminate cements. The higher energy absorption capacity of CAC pastes can help to partially mitigate the spalling [30]. Other factors, however, such as the compactness of the paste’s microstructure, are critical. The higher the compactness, the greater the risk of spalling [31]. One possible solution to mitigate the spalling is the incorporation of fibres in the cementitious matrix. These fibres permit the formation of microracks, which may depressurize the porous cavities up to 50% more as compared to samples without fibres. Then, the mechanical capacity of the paste is sufficient to withstand the pressure of steam in surface areas, avoiding spalling [32]. Nonetheless, as far as we know, no previous studies have examined the effect of natural fibres on the spalling of CAC pastes.

This paper offers an assessment of the thermal and fire behaviour of composite plates made of nonwoven flax fibre fabrics combined with CAC/MK matrices. The fire behaviour was evaluated using epiradiator and small-scale fire tests while thermal behaviour was assessed using thermogravimetric analysis and by determining the effect of high temperatures on the microstructure, and the mechanical performance under bending deformation of the CAC/MK composites. This study offers new insights regarding the performance and behaviour of these new materials when they are subjected to high temperatures and/or fire.

2. Materials and experimental procedures

2.1. Materials

Calcium aluminate cement (CAC) provided by Grupo Cementos Molins (Barcelona, Spain) and metakaolin (MK) provided by Arcillas Refractarias S.A. (Gijón, Spain) were used to prepare the matrix paste. Their chemical composition in oxide equivalent and their main physical properties are provided in Table 1 and Table 2.

To produce the nonwoven fabric reinforcement, flax fibres (6 cm length), provided by Fibres Recherche Développement of the Technopôle de l’Aube en Champagne (France) were used. The nonwoven fabrics (2 mm thick and 275 g/m² areal weight) were produced as described in previous works [7]. The fabrics were then subjected to a hornification process consisting of 4 wet-dry cycles of oven-drying for 8 h at 60 °C followed by a 16-hour water immersion at 20 °C. The aim of this process is to improve the dimensional stability of the fibres and their durability in the cement matrix [33].

The mechanical properties of the nonwoven fabrics were determined by tensile testing according to the UNE-EN ISO standard 13934-1:2013. The average values of maximum force of these fabrics were 73 ± 4 N and 28 ± 5 N in cross and machine direction, respectively.

2.2. Dosage and composite specimen preparation

10 plates of 300 mm × 300 mm and ~ 10 mm thick with were prepared using CAC paste with MK additions from 0% to 40% w/w. These percentages were selected based on previous studies on CAC mixed with different pozzolans [21,22,34,35]. The initial water/cement ratio was fixed at 2. The composites were prepared using a lamination technique with 5 layers of nonwoven fabrics impregnated with cement paste, compacted by vacuum, followed by compression at 3.3 MPa for 24 h. The final water/cement ratio was 0.45. More details on the procedure can be seen in previous works [6,36]. The laminates were cured in a climatic chamber for 28 days at 20 °C and greater than 95% HR. The final fibre content was approximately 5% of the weight of the final composite. The nomenclature of the moulded plates corresponds to the percentage of substitution of MK with respect to the CAC (0MK, 10MK, 20MK, 30MK, and 40MK correspond to a substitution of 0, 10, 20, 30, and 40 wt% of MK). From the plates, specimens with different dimensions were machined to determine the material’s thermal and fire behaviour.

2.3. Experimental procedures

2.3.1. Characterisation of thermal properties

The thermal conductivity and thermal diffusivity were determined using Quickline-30 equipment from Anter Corporation. This device operates using the transient line source method. The equipment analyses the material’s response to the heat flow variations induced by the probe. Measurements were performed in two overlapped 10 cm × 10 cm specimens with a superficial probe. For comparative purposes, the material’s volumetric density was determined by weighing each sample—with an accuracy of ± 0.01 g—and dividing the mass by its volume, calculated from its respective dimensions—measured with an accuracy of ± 0.1 mm—.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Chemical composition in oxide equivalent of calcium aluminate cement (CAC) and metakaolin (MK).</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃ (%)</td>
<td>CaO (%)</td>
</tr>
<tr>
<td>CAC</td>
<td>41.5</td>
</tr>
<tr>
<td>MK</td>
<td>39.4</td>
</tr>
</tbody>
</table>
A specimen of 40 mm × 50 mm was placed on a metallic grid 3 cm underneath a 500 W heating source, implying a heat flux of 3 W/cm² on the material. If the sample ignites during the 5 min of the test, the radiator must be removed and returned once the flames have extinguished. The parameters to be determined with this test are the number of ignitions (N₀), the average time of flame persistence, and the sample’s weight loss during the test.

2.3.3. Small-scale fire resistance tests

The effect of high temperatures on the properties of the plates was assessed using a Hobersal JM3-15 oven, as illustrated in Fig. 1. Samples of 0MK and 40MK, of 100 mm × 100 mm × 10 mm, were placed on the oven door with one of the sides exposed to the standard temperature-time curve specified in ISO 834-1:1999 (shown in Fig. 5). During the test, temperatures were measured by attaching k-type thermocouples to the external side of the sample.

2.3.4. Thermogravimetric analysis

Thermogravimetric analysis was performed on the cement matrix of the 0MK and 40MK, reinforced with vegetable fibres. Samples of approximately 10 mg were heated in an open alumina crucible from 25 °C to 950 °C at 20 °C/min with a flux of nitrogen of 60 mL/min.

2.3.5. Mechanical behaviour

To assess the mechanical behaviour of the samples after their exposure to high temperatures (see Table 3), three specimens of each composite were tested following the points of bending configuration. The distance between supports was 100 mm and the crosshead speed was 1 mm/min. The load cell was 3 kN. The mechanical parameters obtained from the force versus displacement curve were the limit of proportionality (LOP), modulus of rupture (MOR) and modulus of elasticity (MOE), obtained following the same procedure used in previous works [37]. The results were statistically analysed using an analysis of variance (ANOVA) with Tukey HSD test performed with R software [38].

Table 2

<table>
<thead>
<tr>
<th>Material</th>
<th>Loss on ignition (1050 °C) [%]</th>
<th>D100 [µm]</th>
<th>D50 [µm]</th>
<th>Density [g/cm³]</th>
<th>Specific surface area [Blaine] [cm²/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAC</td>
<td>1.410</td>
<td>70</td>
<td>–</td>
<td>3.2</td>
<td>3200</td>
</tr>
<tr>
<td>MK</td>
<td>0.078</td>
<td>50</td>
<td>5</td>
<td>2.54</td>
<td>10,971</td>
</tr>
</tbody>
</table>

Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thermal Conductivity [W/(m·K)]</th>
<th>Thermal diffusivity [10⁻⁶ m²/s]</th>
<th>Volumetric mass density [kg/m³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0MK</td>
<td>0.840 ± 0.006</td>
<td>0.510 ± 0.006</td>
<td>1606</td>
</tr>
<tr>
<td>10MK</td>
<td>0.860 ± 0.006</td>
<td>0.560 ± 0.006</td>
<td>1869</td>
</tr>
<tr>
<td>20MK</td>
<td>0.740 ± 0.010</td>
<td>0.520 ± 0.010</td>
<td>1690</td>
</tr>
<tr>
<td>30MK</td>
<td>0.710 ± 0.015</td>
<td>0.500 ± 0.006</td>
<td>1467</td>
</tr>
<tr>
<td>40MK</td>
<td>0.650 ± 0.006</td>
<td>0.430 ± 0.012</td>
<td>1386</td>
</tr>
</tbody>
</table>

2.3.6. Microstructure

To analyse the effects of exposure to high temperatures on the microstructure, the cross-sections of the specimens after the bending tests were observed using a scanning electron microscopy (SEM). Samples of approximately 8 mm × 8 mm were coated with epoxy resin, polished down to 0.1 µm, and coated with carbon. Images were taken using a JSM-6300 (JEOL, Japan) at 10 kV.

To observe the changes in the microstructure of the cement matrix, back scattered electron images (BSEM) were taken from polished and epoxy resin-coated samples. A BSEM-JSM-7001F (JEOL, Japan) microscope equipped with an energy dispersive X-ray spectrometry (EDS), model Link ISIS-200 (Oxford Instruments, United Kingdom) was used.

3. Results

3.1. Thermal conductivity and diffusivity

Table 4 shows the values of some thermal properties of the composites. It is revealed that thermal conductivity decreases with the MK content, which may be of great interest for increasing the insulating effect of façade panels. This phenomenon can be attributed to several effects, such as differences in the sample’s porosity (Fig. 9d and 10d)—which are related to differences in density—, the morphology of MK particles—which present the form of lamellar groups, resulting in greater difficulty in heat conduction—and, differences in the microstructure—the presence of different phases or different contents—and, this is also consistent with the diffusivity values, which follow the same pattern.

3.2. Epiradiator test

During the epiradiator test, the specimens tested did not show any ignition. This suggests that the presence of the vegetable fibres did not lead to the appearance of flames or smoke. Fig. 2 shows images of the original side (left) and the side exposed to the radiation (right) for the 0MK sample. The evolution of the temperature reached on the surface during the test is shown in Fig. 3. The tested sample presented some cracks on the surface, as shown in Fig. 2b, but without a significant detachment of material (chipped pieces).

The average weight loss of the irradiated samples was 13.9%. This loss is related to the sample’s dehydration and the transformation of certain CAC-hydrated compounds into oxides, due to the high temperatures reached (above 400 °C). These transformations simultaneously lead to a volume reduction of the specimens. The volume reduction, attributed to both the transformation of CAH₁₀ and C₂AH₆ into oxides

Fig. 1. Oven used for the small-scale fire resistance tests.
and the transformation of AH₈, caused some cracks on the surface of the samples, leaving a pattern similar to the retraction on clay pastes, but without any loss of small pieces of the material surface. The ability of this material to maintain its integrity may be related to the bridging effect of the fibre reinforcement. On the other hand, there was no material loss by spalling. The resistance of the CAC hydrated phases. Compared with the surface images shown in Fig. 2, in this case, cracks are thinner. This is because the epiradiator test has a much greater effect on the irradiated surface (which rapidly loses water), while the unexposed surface does not reach high temperatures. As a result, the shrinkage of both sides is very different, leading to more open cracks. Nonetheless, in the small-scale fire resistance test, both sides reach temperatures that are high enough to avoid such a deformation between specimen sides. As for the 40MK sample, it showed a cracking pattern (Fig. 4c and 4d) with more separated and thicker cracks on both sides, although the unexposed side presented a central zone with no visual cracks. This could be related to the loss of water of MK at higher temperatures than 850 °C. As can be seen in Fig. 5, the temperature of the exposed side may have reached temperatures much higher than 850 °C, while the centre of the outer part may not have reached 800 °C. Therefore, a differential deformation may have occurred between those areas where the temperature dehydrated the MK as compared to the areas without MK dehydration.

Fig. 5 shows the evolution of the temperature of the unexposed sides for the 0MK and 40MK samples during the small-scale fire resistance test. As observed, the temperature curves reveal certain differences between the two samples.

Regarding the plateau observed around 100 °C, it is seen that the plateau is shorter for the 0MK sample than for the 40MK sample. The 0MK sample loses interstitial water between the 13th and 18th min of the test (Fig. 5b, a-b), with the external temperature remaining constant between 93 °C and 94 °C. Nonetheless, for the 40MK sample—despite beginning to dehydrate at the same time, approximately at minute 13—the water loss ends around minute 31, and it takes place in two stages, as highlighted by the two steps. In the first plateau (Fig. 5b, 1–2), between the 14th and 19th min, the temperature is maintained between 93 °C and 98 °C, which may be attributed to the loss of water as explained in the 0MK sample. In the second plateau (Fig. 5b, 3–4), between the 22nd and 31st min, the external temperature is maintained between 113 °C and 126 °C. It should be mentioned that at minute 31, the external temperature of 126 °C contrasts with the 847 °C of the oven. Therefore, the temperature throughout the sample is expected to be higher. This second plateau can be attributed to the dehydration of the MK—as a result of the type of lamellar particles of the MK that generates an interlaminar porosity in the form of capillary slots [39]—and/or to the dehydration of some hydrated compounds formed only in the sample containing MK, such as the strätlingite.

After these plateaus, both samples have an inflection point on the slope (Fig. 5b, points c and 5), which may suggest the end of the dehydration of C₆H₇O₃ and C₂AH₆ phases. However, both samples have similar behaviour (parallel temperature curves consistent with the ISO 834–1 curve), with a delay existing in the two samples until 700 °C, when the total dehydration of both samples takes place. Due to this delay, the 0MK sample reaches 450 °C on the unexposed side at minute 41, while the 40MK sample reaches this temperature at minute 51. In addition, when the 40MK sample reaches 126 °C, at minute 31, the 0MK sample reaches 263 °C on the unexposed side.

As for the change observed at approximately 720 °C in the 40MK sample, this variation can be attributed to the end of the dehydration process caused by the AH₈ gel that was absorbed by the MK lamellar...
Particles. As explained in Section 3.7, although free AH$_3$ undergoes dehydration at lower temperatures, the lamellar structure of MK favours the presence of interlayer AH$_3$, which could be delaying its dehydration.

3.4 Thermogravimetric analysis

Fig. 6 shows the TGA curves and the corresponding derivatives (DTGA). The first decomposition step (I) observed in said curves corresponds to the loss of interstitial water by evaporation. It is evident that this loss begins at a lower temperature in the 0MK sample as compared to the 40MK sample ($50^\circ$C and $68^\circ$C respectively), which may be explained by the differences in the microstructure due to the MK incorporation. Once this water is lost, the dehydration of other phases —such as AH$_3$ gel, CAH$_{10}$, and C$_2$AH$_8$— begins. In this second decomposition step (II), the 0MK sample presents the maximum loss at $146^\circ$C, while the maximum loss for the 40MK sample takes place at $172^\circ$C. This dissimilar behaviour could be related to the presence of the strätlingite phase, resulting from the addition of MK. In this sense, the displacement observed in the DTGA curve for the 40MK sample is consistent with the higher dehydration temperature and water content of strätlingite, since the C$_2$AH$_8$ in the 0MK sample can lose 135 g/mol of water, while the strätlingite —only expected in the 40MK sample— would lose 144 g/mol [23].

In a third step (III), the AH$_3$ crystalline and C$_2$AH$_8$ phases are dehydrated at similar temperatures for both 0MK and 40MK samples ($269^\circ$C and $281^\circ$C for AH$_3$, and $279^\circ$C and $289^\circ$C for C$_2$AH$_8$, all respectively). Despite the similarity of the nature of these compounds in both specimens, the 40MK sample presents a lower content of these phases than the 0MK sample, due to the formation of strätlingite. As explained in the introduction, CAH$_{10}$ is the metastable phase that results in C$_2$AH$_6$ and AH$_3$. Therefore, this difference (observed in the magnification in Fig. 6) is consistent with the formation of strätlingite to the detriment of CAH$_{10}$, implying a lower content of the metastable phase to be further transformed into C$_2$AH$_6$ and AH$_3$.

Finally, in a fourth step (IV), the dehydration of interlayer AH$_3$ takes place at around $690^\circ$C. This is consistent with the change observed in the previous section, which will be further explained in Section 3.7.

3.5 Effect of exposure to high temperatures on the mechanical performance of the composites

This section focuses on the effect of exposure to high temperatures on mechanical behaviour: fracture behaviour, on the one hand, and LOP, MOR, and MOE, on the other hand. Fig. 7 presents the typical bending curves obtained for all of the samples having dosages between 0% MK and 40% before and after their exposure to several temperatures (for the sake of clarity, hereafter samples will include the exposure temperature in the nomenclature). Table 5 summarises the LOP, MOR and MOE results obtained from the mechanical characterisation, as well as the Tukey HSD test groups resulting from their statistical analysis.

3.5.1 Effect of exposure to high temperatures on the fracture behaviour

For the samples that were not exposed to high temperatures, the reinforcing effect of the fibres permits relative deformation values of
over 10%. The curves reveal four different stages. Firstly, there is a high slope, until the appearance of the first crack (LOP), which is primarily related to the strength of the matrix, given that the modulus of elasticity of the vegetable fibres is much lower than that of the cement. Secondly, after reaching the LOP there is a lower slope, characterised by a sawtooth wave shape, corresponding to the formation of cracks on the bottom side of the sample. In this case, both the matrix and the fibres contribute to the strength of the composite: the matrix contributes to the strength of the non-cracked zones, and the fibres to the strength of the cracked ones. In the third stage, the stress between cracks does not exceed the tensile strength of the matrix. Therefore, there is no further crack formation. However, deformation increases due to crack thickening. At this stage, the contribution to strength is primarily made by the reinforcement. Finally, the fourth stage begins with crack thickening due to the failure of the nonwoven fabric reinforcement, also producing a local deformation that leads to the fracture of the specimen. This type of fracture is similar to that obtained in samples reinforced with long fibres [40,41].

After the exposure of the material to 250 °C, the bending behaviour changes as compared to the unexposed samples. In this case, the curves only present three stages (see Fig. 7b). First, they show the initial slope until the LOP, as observed in the previous case, suggesting similar behaviour of the matrix in both cases. Thus, for exposure up to 250 °C, the matrix maintains its bending behaviour. As indicated in the introduction, at 250 °C, the interstitial water of the matrix has evaporated, the aluminium gel has dehydrated and a transformation of gibbsite in boehmite has taken place. However, these transformations have not caused a significant loss of the matrix’s strength. In the second stage, the crack thickening of only one single crack is observed, leading to lower deformation values. Finally, the failure of the fibres is observed. The curves in Fig. 7b reveal that the effect of the fibre reinforcement depends on the content of MK. As the MK content increases, the maximum strength decreases but the deformation increases. This type of fracture is similar to that occurring with short-fibre reinforcements, such as pulp fibres [42-44].

Composites exposed to higher temperatures (450 °C and 950 °C) present brittle behaviour, with a negligible effect of reinforcement. Once the first crack occurs, the material breaks suddenly. The composite strength is seen to decrease with the increase in exposure temperature and with the increase in MK content. In fact, all of the samples exposed to 950 °C with a MK content of 40% were broken during test preparation or during pre-loading. This type of fracture is similar to that of unreinforced cements [44].

3.5.2. Effect of exposure to high temperatures on the LOP, MOR and MOE values

As previously mentioned, the LOP is attributed to the mechanical behaviour of the matrix. The LOP values and Tukey HSD test groups shown in Table 5 reveal non-significant differences between the 20 °C and 250 °C samples when MK content is equal (0MK-20 °C = 0MK-
Fig. 7. (a) Comparative plot of the representative bending curves of the samples with different MK dosages (from 0% to 40%) at different exposures to high temperatures: unexposed (grey), exposure to 250 °C (blue), 450 °C (green) and 950 °C (red). To offer a clearer visualisation, (b), (c), and (d) are magnifications of the curves for materials exposed to 250 °C, 450 °C and 950 °C, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 5
Average values, (standard deviations) and Tukey HSD test groups for the limit of proportionality (LOP), modulus of rupture (MOR), and modulus of elasticity (MOE) of the composite materials unexposed (20 °C) and after exposure to 250 °C, 450 °C, and 950 °C.

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</tr>
</thead>
<tbody>
<tr>
<td>0MK-20 °C</td>
<td></td>
<td>8.52 (1.39)</td>
<td>ab</td>
<td>18.71 (1.77)</td>
<td>a</td>
<td>1.11 (0.34)</td>
<td>a</td>
</tr>
<tr>
<td>10MK-20 °C</td>
<td>20</td>
<td>8.57 (0.86)</td>
<td>ab</td>
<td>16.74 (1.61)</td>
<td>ab</td>
<td>1.01 (0.63)</td>
<td>ab</td>
</tr>
<tr>
<td>20MK-20 °C</td>
<td></td>
<td>7.63 (1.43)</td>
<td>abcd</td>
<td>10.95 (1.24)</td>
<td>cd</td>
<td>0.40 (0.18)</td>
<td>abc</td>
</tr>
<tr>
<td>30MK-20 °C</td>
<td></td>
<td>7.78 (0.74)</td>
<td>abcd</td>
<td>13.83 (1.74)</td>
<td>bc</td>
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<tr>
<td>40MK-20 °C</td>
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<td>5.37 (1.21)</td>
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<td>10.75 (1.84)</td>
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<td>0.40 (0.18)</td>
<td>abc</td>
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<tr>
<td>0MK-250 °C</td>
<td></td>
<td>9.55 (1.51)</td>
<td>a</td>
<td>9.66 (1.50)</td>
<td>de</td>
<td>0.92 (0.75)</td>
<td>ab</td>
</tr>
<tr>
<td>10MK-250 °C</td>
<td>250</td>
<td>8.01 (1.14)</td>
<td>abc</td>
<td>8.85 (1.43)</td>
<td>de</td>
<td>0.35 (0.39)</td>
<td>abc</td>
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<td>20MK-250 °C</td>
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<td>7.25 (0.98)</td>
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<td>def</td>
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<td>abc</td>
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<td>30MK-250 °C</td>
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<td>6.35 (0.49)</td>
<td>bcd</td>
<td>6.43 (0.46)</td>
<td>ef</td>
<td>0.07 (0.04)</td>
<td>bc</td>
</tr>
<tr>
<td>40MK-250 °C</td>
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<td>5.49 (1.09)</td>
<td>cde</td>
<td>5.56 (1.05)</td>
<td>fg</td>
<td>0.07 (0.04)</td>
<td>bc</td>
</tr>
<tr>
<td>0MK-450 °C</td>
<td></td>
<td>5.09 (0.66)</td>
<td>de</td>
<td>5.08 (0.66)</td>
<td>fg</td>
<td>0.63 (0.54)</td>
<td>abc</td>
</tr>
<tr>
<td>10MK-450 °C</td>
<td>450</td>
<td>2.94 (0.92)</td>
<td>ef</td>
<td>2.94 (0.92)</td>
<td>ghi</td>
<td>0.30 (0.26)</td>
<td>abc</td>
</tr>
<tr>
<td>20MK-450 °C</td>
<td></td>
<td>2.08 (0.57)</td>
<td>fg</td>
<td>2.08 (0.57)</td>
<td>hi</td>
<td>0.28 (0.24)</td>
<td>abc</td>
</tr>
<tr>
<td>30MK-450 °C</td>
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<td>1.75 (0.28)</td>
<td>fg</td>
<td>1.75 (0.28)</td>
<td>i</td>
<td>0.23 (0.20)</td>
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</tr>
<tr>
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<td>1.10 (0.53)</td>
<td>i</td>
<td>0.11 (0.10)</td>
<td>abc</td>
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<tr>
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<td>1.71 (0.41)</td>
<td>i</td>
<td>0.19 (0.18)</td>
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<td>fg</td>
<td>1.49 (0.93)</td>
<td>i</td>
<td>0.18 (0.25)</td>
<td>abc</td>
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<td>i</td>
<td>0.10 (0.10)</td>
<td>bc</td>
</tr>
<tr>
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<td>1.07 (0.20)</td>
<td>i</td>
<td>0.05 (0.08)</td>
<td>bc</td>
</tr>
<tr>
<td>40MK-950 °C</td>
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<td>g</td>
<td>0.00 (0.00)</td>
<td>i</td>
<td>0.00 (0.00)</td>
<td>c</td>
</tr>
</tbody>
</table>

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250 °C, 10MK-20 °C = 10MK-250 °C, etc.). Therefore, it can be concluded that exposure to 250 °C did not produce significant damage in the matrix, as seen in the previous section. Moreover, the LOP average values decrease with the MK content. This can be explained by the fact that the MK does not react with the hydration compounds of the CAC, having an effect that is similar to that of an inert aggregate [9]. Only extremely different compositions present significant differences after exposures of up to 450 °C (for 20 °C, 0MK ≠ 40MK; for 250 °C, 0MK ≠ 30-40MK; and for 450 °C, 0MK ≠ 20–30-40MK). This suggests that the MK worsens the mechanical behaviour of the matrix after exposure to high temperatures, increasing the differences between the samples with 0MK matrix from the others when increasing the exposure temperature. On the contrary, after exposure to 950 °C, no significant difference is found in LOP values, regardless of the MK content. The mechanical strength of the matrix is clearly lower as compared to the unexposed samples. This suggests a degradation of all of the matrices due to the high temperature.

Differences between the LOP and MOR values decrease as the exposure temperature increases, suggesting a degradation of the reinforcement with temperature. In fact, fibres had no effect after 450 °C.

Fig. 8. SEM images (50x) of the fracture surface of the samples with minimum and maximum MK content (0MK and 40MK) unexposed (20 °C) and after exposure to 250 °C, 450 °C, and 950 °C.
Although the MOR values are reduced with the increase of MK content and the exposure temperature, the Tukey HSD test reveals non-significant differences between samples at 450 °C and 950 °C. It should be noted that, except for the 0MK-450 °C sample, this is consistent with the aforementioned lowering of mechanical properties following thermal exposure due to the incorporation of MK.

For the MOE values, a similar trend is observed, with these values being reduced with the increase in exposure temperature and MK content, although variations are non-significant, as revealed by the overlapping of Tukey HSD test groups.

3.6. Effect of exposure to high temperatures on the nonwoven fabric reinforcement

Fig. 8 shows the SEM micrographs of the fracture surfaces for the 0MK (left images) and 40 MK (right images) specimens tested under bending force. These micrographs agree with the mechanical behaviour observed.

As for the unexposed samples (20 °C), the fracture micrograph of the 0MK-20 °C sample (Fig. 8a) shows fibre pull-out with major disaggregation of the matrix near the fibre layer (see disaggregated particles marked with yellow), although the fibres do not present clear signs of degradation. This is consistent with the observed mechanical behaviour of the material, which presented good strain hardening since both the degradation. This is consistent with the observed mechanical behaviour of the material, which presented good strain hardening since both the degradation.

The curve of the samples in Fig. 7 reflects this cracking behaviour (disaggregated matrix particles) in the form of a sawtooth curve that appears as the load increases. For the 40MK-20 °C sample (Fig. 8b), a higher matrix disaggregation is observed (see disaggregated particles marked with red arrows), consistent with the larger sawtooth area previously observed in Fig. 7.

At 250 °C, the mechanical performance of the fibres of both samples (0MK-250 °C and 40MK-250 °C in Fig. 8c and d, respectively) decreases since the cellulose begins to degrade. Thus, the fibres break very close to the surface. The fracture micrographs show fibre pull-out but matrix disaggregation is lower or non-existent, with those of the 40MK-250 °C fibres (Fig. 8d) being slightly longer than those of the 0MK-250 °C fibres (Fig. 8c). The traction cracks propagate from the bottom plane of the specimen throughout the section and are retained by the nonwoven reinforcement layer until fibre’s failure, when the cracks can thrive to the next layer of reinforcement, which retains now its advance, and so it continues, layer by layer, until the total section break. Hence, the reinforcing effect is restricted to the fibre-matrix adhesion, with no contribution by the nonwoven structure. This is consistent with the mechanical behaviour, similar to that of pulp-reinforced cements. In the bending curve (Fig. 7), it is observed that the reinforcing effect takes place just after the first crack, where the load capacity increases, until adhesion is lost and the fibre and section are broken. For the 40MK-250 °C sample, the larger strain values of the bending curve in Fig. 7 agree with the presence of longer fibres (Fig. 8d).

For higher temperatures, at 450 °C, the fibre has almost decomposed and there is no reinforcing effect. Some carbonized fibres remain adhered to the matrix (see arrows on the correspondent images in Fig. 8e and 8f). However, at 950 °C the fibre has completely disappeared and only the shape of fibre-prints can be observed at the fracture surface (Fig. 8g and 8h).

On the other hand, only concerning the fibres, Fig. 11a and 11b reveal that most of the reinforcing fibres are still bonded to the matrix, but in an initial fibre-degradation state, after exposure of the composites to 250 °C. These figures also show fibre shrinkage—produced by water loss—and local debonding. This phenomenon is consistent with the loss of tenacity observed in the strength-strain curves, although the post-cracking reinforcing capacity is maintained. At 450 °C and 950 °C, fibre degradation is complete (holes with some fibre ashes are observed in Fig. 11c, 11d, 11e and 11f), causing the full loss of reinforcement capacity, as expected. These results are also consistent with the brittle fracture observed in samples tested after exposure to 450 °C and 950 °C.

As expected, the incorporation of fibres prevented the spalling effect. Up to 250 °C, the fibres maintain their integrity despite a reduction in strength (caused by the partial decomposition of the fibres). However, unlike other fibres such as polypropylene or steel, which are solid and waterproof, flax fibres are hollow and permeable. This facilitates the transport of steam through the material and, consequently reduces the pressure that could lead to surface fracture of the composite. At temperatures exceeding 250 °C, the fibres are decomposed and carbonized, considerably increasing the matrix’s porosity, although also permitting steam diffusion and hence, reducing pressure. These results are in line with previous findings [32].

3.7. Effect of exposure to high temperatures on the cement matrix microstructure

Figs. 9 and 10, respectively, show the representative BSEM micrographs of the 0MK-20 °C and 40MK-20 °C composites (after 28 days curing, unexposed to high temperatures) at various magnifications, and the corresponding identification of the cement phases by EDX.

Micrograph 9a offers a general view of the 0MK-20 °C sample, in which it is possible to observe several anhydrous particles (light grey), hydrated phases of the matrix (medium grey), and the fibres (dark grey). Hydrated-phase rich zones are also shown to surround the fibres, consistently with the water retention effect of cellulose fibres. The anhydrous phase (Fig. 9d, SP1) may appear to be a calcium aluminate particle (monocalcium aluminate (CA), but the presence of Fe, TiO2, SiO2, and MgO indicates that it could be a Ca2Fe2-O-F phase type. More specifically, it could be a spinel phase. As for the hydrated phases (Fig. 9d, SP2 and SP3), the first one (SP2) could be related to C2AH8 hexagonal crystals, based on the observation of typical cliffs of inter-laminar spaces. The second one (SP3), more homogeneous, could be an AH3 gel. Finally, the SP4 spectrum in Fig. 9d indicates a high presence of carbon, confirming that these are the cellulose fibres.

A general view of the 40MK-20 °C sample at 28 days of curing is presented in Fig. 10a. Unlike the previous sample, a lower content of anhydrous particles (light grey) and a higher content of hydrated phases (medium grey) are found. In this case, there was no observed presence of a C2AH8 phase or porosity derived from the transformation of C2AH8 into C2AH6. This is consistent with the transformation of CASH2 and MK’s amorphous silica into C2ASH2. However, in micrograph 10d, numerous MK particles (SP3 spectrum) may be observed, having a grey colour that is similar to the hydrated phases. Therefore, in this case, the lower proportion of anhydrous particles may be related to the substitution of 40% of CAC by MK, and not directly with a higher content of CAC-hydrated phases. In fact, Fig. 10d shows these MK particles (indicated by yellow dotted line) embedded in hydrated phases, with CAC-hydrated gel (AH3 gel) intercalated in the MK lamellar structure. The darkest parts correspond to the fibres. As in the 0MK-20 °C sample, a higher content of hydrated CAC phases is observed in the surroundings of the fibres.

The changes on the matrix by the effect of exposure to high temperatures (250 °C, 450 °C and 950 °C) can be seen in the BSEM images in Fig. 11. In this figure, certain details of specific areas of the matrix at higher magnifications are also shown, as well as some EDX analysis of specific particles.

After exposure to 250 °C, the presence of MK induced different changes on the degradation of the matrix compounds, with respect to the 0MK matrix, depending on the temperature. As shown in the TGA curves (Fig. 6), at this temperature there is a total mass loss of 8.5% in the 0MK-250 °C sample and of 9.9% in the 40MK-250 °C sample. This mass loss is related to the evaporation of the interstitial water present in both samples. Additionally, the higher mass loss of the 40MK-250 °C sample, as compared to that of the 0MK-250 °C sample, can be explained by the dehydration of the C2ASH2 phase (strätlingite), which occurs below 250 °C. Moreover, a higher porosity is observed in the 40MK-250 °C
Fig. 9. BSE-SEM images of the 0MK-20 °C sample at different magnifications and their corresponding EDX spectra.

Fig. 10. BSE-SEM images of the 40MK-20 °C sample at different magnification (a, b, d) and the EDX spectra (c) corresponding to the points marked in image d.
sample due to the dehydration of this phase. Comparing the 0MK-$20^\circ$C and 0MK-$250^\circ$C samples, the disappearance of the C$_2$AH$_8$ crystals may be observed (see Fig. 9d, SP2). They may have transformed into C$_2$AH$_6$.

In the case of the 40MK-$20^\circ$C and 40MK-$250^\circ$C samples, the agglomerates of MK particles with CAC hydrated gel (AH$_3$ gel, possibly) present no differences at temperatures of 20 $^\circ$C (see marked particles in Fig. 10d) and 250 $^\circ$C (see magnification in Fig. 11b). The spectrum of SP1 in Fig. 11b confirms that this mixture of MK and CAC gel particles remained stable, despite exposure to 250 $^\circ$C.

After exposure to 450 $^\circ$C, the total mass loss is 16.3% for the 0MK-$450^\circ$C sample, and 17.7% for the 40MK-$450^\circ$C sample, suggesting a similar relative mass loss of 7.8% in both cases, as compared to that occurring at 250 $^\circ$C. For the 0MK-$450^\circ$C sample, the dehydration of most of the CAC hydrated phases has taken place, while the polyphasic anhydrous particles maintain their original appearance. This dehydration generates a high porosity in the matrix, especially as compared to 0MK-$250^\circ$C sample. In the 40MK-$450^\circ$C sample, in addition to the dehydration of the CAC compounds, it is possible to observe the presence of the same MK/AH$_3$ gel agglomerates that were previously observed in the 40MK-$250^\circ$C sample. The SP2 spectrum denotes the same chemical composition and is very similar in appearance. It appears that the AH$_3$ gel, present in-between the lamellar structure of MK, also remains stable at this temperature, although it does not provide an increased matrix strength.

After the exposure of the samples to 950 $^\circ$C, no significant changes are observed in the 0MK-$950^\circ$C sample. The total mass loss at this temperature is 18.1% and, as seen in Fig. 11, the appearance of the samples is very similar (0MK-$450^\circ$C vs. 0MK-$950^\circ$C). However, as seen in detail at higher magnification, the pores have a larger size and are interconnected by cracks. This may justify the 66.4% decrease in strength, despite the small relative mass loss between 450 $^\circ$C and 950 $^\circ$C (1.8%). On the other hand, the 40MK-$950^\circ$C sample has a total mass loss of 20.3% for this temperature and therefore, a relative mass loss of 2.5% with respect to 450 $^\circ$C. This difference in the relative mass loss results

![Fig. 11. BSE–SEM images of the 0MK (left) and 40 MK (right) samples after exposure to 250 °C, 450 °C, and 950 °C. Yellowed areas correspond to the magnification shown in each sample.](image-url)
from the last transformation of the 40MK sample at approximately 650 °C-700 °C, as evidenced in the DTGA (Fig. 6-IV). The appearance of the matrix has varied substantially and more pores having a lenticular form are observed. On the image at higher magnification (Fig. 11f), some MK agglomerated particles can still be observed, although without the gel between them, which has been dehydrated, causing additional porosity within the MK particles. The greater mass loss may be due to the dehydration and transformation of this gel, previously trapped between MK particles.

4. Conclusions

The following conclusions can be reached from this study:

- The addition of MK to CAC pastes increases the insulation and thermal diffusivity of the material and, at the same time, decreases the density of the composite material. These effects are beneficial for the use of the composites as cladding materials in ventilated façades, as proposed in this paper.
- The material, for all of the composites studied, did not generate any smoke or flames and did not suffer from spalling or a loss of integrity in any of the thermal and fire tests performed, even when exposed to temperatures higher than 1000 °C for more than 135 min in some of these tests.
- The incorporation of MK induces a thermal delay of approximately 10 min between the exposed and unexposed sides in the fire tests. This delay is relevant since it suggests that, for a given time, the temperature of the unexposed side is 130 °C lower than the side exposed to the fire.
- As expected, the material’s exposure to high temperatures leads to the reduction of its mechanical performance. Nonetheless, the fibres maintained their reinforcement capacity up to 250 °C, with the matrix’s mechanical performance remaining up to this temperature in the 0MK and 40MK samples, despite the dehydration of C₃ASH₃ phase. After exposure to 450 °C, a reduction of the matrix’s strength by up to 50% of the initial strength was observed. Upon exposure to 950 °C, the decrease was up to 25% of the initial strength. In general, composites with more MK had lower strength, although they had similar or higher relative deflections.
- The incorporation of MK in the paste produced distinct phenomena: a) the formation of a C₃ASH₃ phase, which increased the thermal delay; and b) the formation of a different morphology with agglomerates of MK lamellae with interlamellar AH₃ gel. The interlamellar AH₃ gel remained hydrated until approximately 700 °C, although it apparently has no effect on the enhancement of the material.

Therefore, considering the results of the material’s mechanical, thermal, and fire behaviour, it may be concluded that the composites proposed in this work—based on calcium aluminate cement, with and without the addition of metakaolin, and reinforced with vegetable fibres—are a good alternative to stone or ceramic plates in ventilated façades.

CRediT authorship contribution statement

L. Gonzalez-Lopez: Investigation. J. Claramunt: Conceptualization, Methodology, Resources. L. Haurie: Methodology, Resources, Writing - review & editing. H. Ventura: Methodology, Writing - original draft. M. Ardanuy: Conceptualization, Methodology, Resources, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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