Assessment of the physical-mechanical performance of magnesium oxide-based fiber cement submitted to accelerated carbonation

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Abstract

In the pursuit of unconventional binders that can reduce energy consumption in production, magnesium oxysulfate (MOS) cement emerges as a viable alternative. Moreover, carbon dioxide (CO_2) has been employed in the curing process of certain MOS cement products, such as magnesia fiber cement, due to its capacity to enhance their performance. This study aims to assess the impact of pre-curing prior to accelerated carbonation on the physical-mechanical properties of magnesium oxide fiber cement boards. These boards were manufactured using the Hatschek process simulation and subjected to pre-curing periods of 24, 48, and 72 h post-production. The relationship between microstructural alterations and the physical-mechanical properties was examined through analyses including water absorption, apparent porosity, apparent density, four-point bending tests, X-ray diffraction, and scanning electron microscopy analyses. The results indicated that pre-curing had an influence on the physical-mechanical attributes of the manufactured boards. After 72 h, the carbonated materials exhibited a decline in mechanical performance, a phenomenon attributed to the carbonation reactions between CO_2 and the hydration products responsible for enhancing the mechanical strength of the cementitious materials.

Keywords: MOS cement, accelerated carbonation, magnesia fiber cement, Hatschek process simulation, carbon capture.

INTRODUCTION

The past few decades have witnessed noteworthy advancements and renewed interest in alternative materials intended for application within the construction sector. Notably, magnesia-based cements have garnered substantial attention in this context. Brazil's position as a prominent global magnesite ($MgCO_3$) producer, serving as the principal precursor for magnesium oxide (MgO), has come to the fore in recent years [1]. However, the extent of research concerning construction materials founded on MgO remains constrained. This underscores the imperative for additional comprehensive investigations aimed at optimizing their practical implementation within the construction domain. Like the production of ordinary Portland cement (OPC) from limestone, the process of obtaining magnesium oxide (MgO) involves the heating of magnesite. Notably, the calcination temperature required for magnesite (approximately 750 °C) is significantly lower than the temperature employed in OPC production (approximately 1450 °C) to achieve reactive MgO. This divergence in calcination temperatures contributes to a marked reduction in energy consumption throughout the process [2, 3]. However, it is essential to highlight that the production of reactive MgO is accompanied by a substantial release of carbon dioxide (CO_2) emissions [4]. Given the recognized greenhouse effect associated

with CO_2 [5], it becomes imperative to incorporate carbon capture methodologies within the manufacturing framework of MgO-based cements [6]. The present study discusses magnesium oxysulfate cement (MOS), an unconventional binding material synthesized via the chemical interaction between magnesium oxide (MgO) and a magnesium sulfate ($MgSO_4$) solution, as previously elucidated elsewhere [7-9]. This distinctive composite exhibits several commendable attributes, including but not limited to, fire resistance, reduced weight, diminished alkalinity, and heightened energy efficiency. Notably, its primary application resides in the realm of lightweight panel manufacturing, as substantiated by other studies [10-12]. Nevertheless, it is imperative to acknowledge that the susceptibility of MOS to environmental factors, notably elevated humidity conditions, precipitates a decline in its structural integrity, thereby imposing constraints on its widespread integration within the construction industry.

The mechanical characteristics of MOS cement are primarily contingent upon the intricate dynamics of hydration reactions and the specific type and relative proportions of the resultant hydration phases within the solidified cement matrix. Within the context of the ternary system encompassing magnesium oxide (MgO), magnesium sulfate ($MgSO_4$), and water (H_2O), four distinct oxysulfate phases become prominent when exposed to temperatures within the range of 30 to 120 °C. These phases are categorized as follows: i) $3Mg(OH)_2.MgSO_4.8H_2O$ (3-1-8 phase); ii) $5Mg(OH)_2.MgSO_4.3H_2O$ (5-1-3 or 5-1-2 phase); iii) $Mg(OH)_2.MgSO_4.5H_2O$ (1-1-5 phase); and

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iv) $Mg(OH)_2.2MgSO_4.3H_2O$ (1-2-3 phase) [13]. These oxysulfate phases, arising from the complex interplay of MgO, $MgSO_4$, and H_2O, significantly influence the mechanical attributes of MOS cement, thereby constituting vital components in its structural behavior and performance. In the context of industrial applications of MOS cements, where concerns such as diminished mechanical strength and compromised water resistance have posed significant challenges, a noteworthy development was reported by Deng [14]. This advancement involved the introduction of chemical additives that engender a novel hydration product, characterized by the capability to enhance both the mechanical robustness and stability of the cement, particularly in environments marked by elevated humidity levels. More recently, in a study conducted by Runcevski et al. [15], an exhaustive examination of the chemical composition and crystallographic structure of this innovative hydration product was undertaken using contemporary analytical techniques. As a result, the researchers made a significant discovery, identifying a fresh MOS phase crystallizing with a stoichiometry of $5Mg(OH)_2.MgSO_4.7H_2O$, denoted as the 5-1-7 phase. The structural attributes of the 5-1-7 phase are instrumental in enhancing the mechanical performance of the cement. This improvement can be attributed primarily to the intricately interwoven, needle-like structures it forms, along with its effective filling capacity within the cement matrix. These attributes collectively underscore the pivotal role played by the 5-1-7 phase in elevating the mechanical properties of MOS cement [16, 17].

An alternative method to enhance the physical and mechanical properties of cementitious products involves the application of accelerated carbonation. This procedure entails a series of chemical reactions characterized by the diffusion of carbon dioxide (CO_2) through the saturated pores of a cement matrix [18]. In pursuit of this objective, it is essential to consider several pivotal parameters that directly impact the velocity and extent of advancement of this phenomenon. Notably, variables such as CO_2 concentration, temperature, and humidity exert direct influence over the pace and depth of the carbonation process. In this regard, the parameters governing the carbonation process, including CO_2 concentration, temperature, and humidity, wield direct influence over the pace and depth of this phenomenon. It is noteworthy that the examination of accelerated carbonation in the context of MOS cements has remained relatively limited. However, recent investigations have yielded promising results, indicating the potential for enhancing mechanical strength, reducing porosity, and mitigating alkalinity through carbonation [10]. These findings hold promise for bolstering the durability of cellulosic fibers embedded within this matrix. As elucidated by Li et al. [19], the integration of CO_2 capture during the curing phase enhances resistance to wet-dry cycling. The outcomes of these studies suggest that magnesium hydroxide and certain basic magnesium oxysulfate phases are neutralized by carbon dioxide, forming magnesium carbonate phases within MOS cement. This transformation results in structures characterized by refined pore networks and increased mechanical strength. Considering the notable reduction in energy consumption associated with MOS cement production [2, 3], the exploration of accelerated carbonation assumes added significance. This focus aligns with broader environmental objectives, particularly those related to carbon capture [20].

The primary objective of this paper is to assess the impact of pre-curing duration (the time preceding carbonation) on the physical and mechanical alterations observed in magnesia fiber cement boards. In accordance with the experimental procedure, a comparative analysis was conducted between fiber-cement boards produced via the Hatschek process simulation without accelerated carbonation (the reference) and boards subjected to pre-curing with accelerated carbonation after 24, 48, and 72 h of production.

MATERIALS AND METHODS

Materials: the MOS based fiber-cement boards were produced with a mixture of magnesium oxide powder (MgO), magnesium sulfate heptahydrate ($MgSO_4.7H_2O$), dolomitic limestone, citric acid, and reinforced with unbleached eucalyptus cellulose fiber. The MgO (Q-MAG-200-AR, AR200, RHI-Magnesita, Brazil) was obtained by controlled calcination of magnesite (natural magnesium carbonate); it had a specific gravity of 3.45 g/cm^3 and a specific surface area (SSA) of 26.71 m^2/g. Magnesium sulfate heptahydrate (commercial-grade, Epsom) was used with a purity of 99.83%. The dolomite limestone (Itaú Limestone, Votorantim Cimentos, Brazil) with a density of 2.79 g/cm^3 was used as a filler in the fiber-cement boards. Citric acid of analytical purity (Labsynth) was used in the mixture in a proportion of 0.50% in relation to the mass of MgO. The cellulose pulp (Suzano Papel e Celulose, Brazil) used was obtained from unbleached eucalyptus paper kraft.

Sample preparation: the fiber cement boards were obtained from an adaptation of the industrial Hatschek process. The cellulose pulp was initially dispersed in a mixture of distilled water and $MgSO_4$ solution with a concentration of 25% (w/v) and 0.50% of citric acid, at 3000 rpm for 5 min. Immediately afterward MgO in a $MgO:MgSO_4$ molar ratio of 10 and dolomitic limestone at 20% of the amount of MgO by mass (previously homogenized) were added, and the mixture was stirred for another 3 min. The paste was transferred to a perforated mold and a vacuum was applied. Subsequently, the board was pressed (3.2 MPa) for 5 min until it reached a thickness of 6-5 mm.

Accelerated carbonation process: to evaluate the effect of carbonation at early ages of curing, the samples were kept in a hermetically sealed environment for 24 h. All samples were exposed to a concentrated CO_2 environment of 20% CO_2 and 60% relative humidity (RH) at 40 °C for 6 h to accelerate the carbonation process in a climatic chamber (EPL-4H, Espec). The boards were carbonated after 24, 48, and 72 h of production and named Carb24, Carb48, and Carb72, respectively. The sample cured without the carbonation process was named Ref.

Characterization of samples: the physical, mechanical, and microstructural characterization of the boards was performed 7 days after molding. The test specimens were cut to dimensions of 160x40x5 mm. A total of 8 test specimens were utilized for the mechanical and physical analyses of the materials produced under varying conditions. ASTM-C948-81 [21] was used to determine the physical properties. Water absorption, apparent porosity, and apparent density were the parameters examined. The water absorption analysis is a method used to determine the extent to which cementitious materials absorb water when immersed in a controlled environment. This analysis involves submerging the samples in water for a specified duration and subsequently measuring the increase in their weight due to water absorption. The results provide insights into the bulk density and total void volume of the specimens, which are crucial factors affecting their durability and performance in various applications. Mechanical characterization was carried out in a universal testing machine (DL-30000, Emic) with a load cell of 1 kN and a 4-point bending fixture (135 mm between bottom supports and 45 mm between top supports), and using a load speed of 5 mm/min. The deflection during the bending test was collected by the deflectometer positioned in the middle span, on the underside of the specimen. The deflectometer (Emic) used had a maximum deformation of 30 mm and an accuracy of 0.0001 mm. The modulus of rupture (MOR), the limit of proportionality (LOP), modulus of elasticity (MOE), and specific energy (SE) were subsequently determined using RILEM's test procedure and the methodology employed by Savastano et al. [22, 23]. To identify phase evolution X-ray diffraction (XRD) and scanning electron microscopy (SEM) were performed on samples extracted before and after each different carbonation conditions. XRD pattern of fiber-cement boards was collected with a diffractometer (LA-60, Horiba) using CuKα radiation generated with a voltage of 40 kV and a tube current of 30 mA between 2θ angle of 10-70° at a rate of 2 °/min. The morphological analyses were performed using an SEM microscope with a field emission gun (XL-30 FEG, Philips).

RESULTS AND DISCUSSION

The results of the mechanical tests for carbonated and non-carbonated fiber cement boards are presented in Table I. It is possible to observe that the carbonation process caused changes in the properties of the materials produced. The carbonated boards, after 48 h of molding, showed average MOR values close to 18.5 MPa, representing an 18% increase compared to the reference material. The carbonation processes carried out after 24 and 48 h resulted in changes in the values of LOP and MOE, which were associated with the increased stiffness of the material during the chemical reactions between the matrix and CO_2 in the system. These reactions promoted the formation of different magnesium carbonates, as shown in Eq. A for magnesite, Eq. B for artinite, and Eq. C for hydromagnesite [24]:
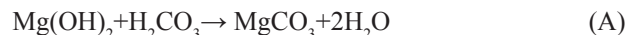
$$Mg(OH)_2 + H_2CO_3 \rightarrow MgCO_3 + 2H_2O \quad\quad (A)$$

$$2Mg(OH)_2 + CO_2 + 2H_2O \rightarrow MgCO_3.Mg(OH)_2.H_2O \quad\quad (B)$$

$$5Mg(OH)_2 + 4CO_2 \rightarrow 4MgCO_3.Mg(OH)_2.4H_2O \quad\quad (C)$$

Table I - Mechanical properties of MOS-based fiber cement boards.

Sample	MOR (MPa)	LOP (MPa)	MOE (GPa)	SE (kJ/m²)
Ref	15.2±1.6	12.4±1.9	9.9±1.2	3.4±0.5
Carb24	13.8±2.9	10.2±1.5	9.9±1.6	2.7±0.3
Carb48	18.5±0.9	14.7±0.9	10.5±1.4	2.9±0.7
Carb72	12.5±2.2	10.8±2.9	8.3±1.2	2.6±0.4

MOR: modulus of rupture; LOP: limit of proportionality; MOE: modulus of elasticity; SE: specific energy.

The formation of these carbonates occurs preferentially in the pores and voids between the matrix and the reinforcement used. The filling of the voids in the material increased its stiffness (increase in MOE) and consequently reduced the specific energy of the carbonated boards (Table I), and modified the typical curves of stress versus flexural strain observed during the load test (Fig. 1). The hydration products formed during MgO-based cement production, such as brucite, exhibit relatively low mechanical strength. However, accelerated carbonation can significantly enhance the mechanical strength of these products. Typical hydrated magnesium carbonate (HMC) phases, including artinite, nesquehonite, and hydromagnesite are commonly encountered in this context [25]. The superior mechanical performance observed in the carbonated materials after 48 h may be attributed to several key factors, such as: i) carbonation is more effective with greater formation of hydration products; after 48 h, there may be a significant increase in the quantity of carbonatable materials compared to those observed after
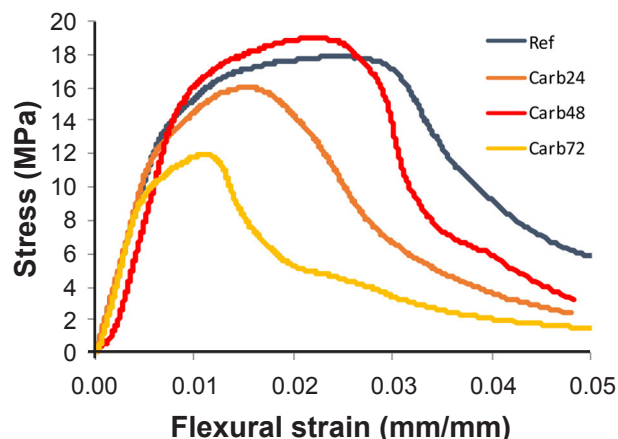

Figure 1: Typical bending test curves of the carbonated and non-carbonated boards.

24 h [26]; and ii) the presence of an adequate amount of water in the material is essential to facilitate carbonation reactions; after 72 h, the material may not retain sufficient moisture to carbonate the hydration products, and hydration reactions might preferentially occur in the compounds responsible for mechanical strength, as is discussed subsequently [27].

Accelerated carbonation caused changes in the physical properties of the materials due to the formation of carbonates (Table II). The formation of these compounds, preferably in the voids and pores, may be associated with the decrease in water absorption values and porosity, observed in all samples. On the other hand, the carbonation products led to an increase in the density of the composites, which may be linked to the improvement in the mechanical performance of the investigated materials.

Table II - Physical properties of carbonated and non-carbonated boards.

Sample	Water absorption (%)	Apparent porosity (%)	Bulk density (g/cm³)
Ref	21.7±3.5	31.5±2.8	1.46±0.01
Carb24	18.1±1.8	27.6±1.8	1.53±0.05
Carb48	17.8±0.8	27.5±0.7	1.54±0.03
Carb72	20.7±1.2	29.5±2.5	1.50±0.05

The crystalline phases formed during the production of carbonated and non-carbonated MOS matrix fiber cements were analyzed by X-ray diffraction, and the results are presented in Fig. 2. Peaks related to the brucite phase (COD 96-100-0055), periclase (COD 96-900-6786), calcite (96-900-9669), and also crystalline phases related to the 5-1-7 phase, responsible for the mechanical strength of the materials produced, can be observed [28, 29]. It was possible to observe that the 5-1-7 phase formed in significant quantities in the materials, which can be associated with the mechanical strength exhibited by these boards. However, a decrease in the intensity of the diffraction peak corresponding to the 5-1-7 phase at angles close to 26.7° 2θ was observed. This decrease suggested that the carbonation process at ages beyond 72 h favored the carbonation of phases responsible for the strength of the materials (5-1-7 phase) and may be associated with the reduction in mechanical strength exhibited by the Carb72 board. Eq. D represents the chemical process responsible for the consumption of the 5-1-7 phase $[5Mg(OH)_2.MgSO_4.7H_2O]$ during curing in a CO_2-rich atmosphere. After the accelerated carbonation process, the peaks corresponding to this phase disappeared, along with a decrease in the intensity of the peaks related to brucite $[Mg(OH)_2]$. The carbonation products were not identified by X-ray diffraction. This may be associated with the formation of carbonation products with low atomic ordering (amorphous). This is possible due to the physicochemical conditions present in the system during the chemical reactions involving the alkaline species and the CO_2 present in the carbonation chamber.

$$(n+1)Mg(OH)_2.MgSO_4.(m+1)H_2O+CO_2 \rightarrow$$
$$MgCO_3+ nMg(OH)_2.MgSO_4.mH_2O \qquad (D)$$
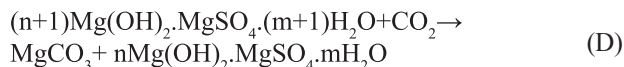
The obtained images by scanning electron microscopy of the materials are presented in Fig. 3. It can be observed that the lignocellulosic reinforcement was dispersed within the material, which was related to the mechanical properties observed in the flexural tests. Fractured fibers were observed in the images (Figs. 3a and 3b), indicating their adhesion to the inorganic matrix and subsequent fracture during mechanical loading. In Fig. 3b, it is possible to observe the presence of voids in regions close to the vegetal fibers. A reduction in the voids was observed in these regions after the accelerated carbonation process (Fig. 3c). This process occurred through the formation of hydration products, which promoted a decrease in the void volume and water absorption of the composites. The presence of flake-like crystals was identified in all samples, which was associated with the formation of $Mg(OH)_2$, the main hydration product of MgO (Fig. 3d). The accelerated carbonation process induced changes in the mechanical properties of the materials, as observed in the results of the physical-mechanical properties. The carbonated sample after 72 h (Carb72) exhibited a decrease in mechanical strength after curing in a CO_2-rich atmosphere. Morphological analysis of this sample revealed the presence of microcracks on the material surface (Fig. 3e). These defects may be responsible for the reduced mechanical resistance observed in the Carb72 boards. The surface analysis of the Carb48 sample is presented in Fig. 3f. Crystals related to $Mg(OH)_2$ were observed, along with needle-shaped crystals associated with the 5-1-7 phase. The occurrence of 5-1-7 crystals in contact with $Mg(OH)_2$ crystals was also reported in previous studies [30], linking the formation of this phase to improved compaction of the cementitious material and corroborating the results of the physical properties of the produced materials.
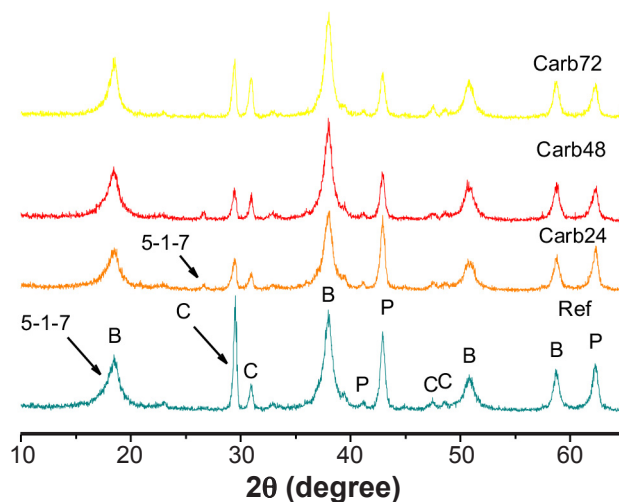

Figure 2: X-ray diffractograms of carbonated and non-carbonated MOS-based fiber cement samples {B: brucite $[Mg(OH)_2]$; C: $CaCO_3$; P: periclase (MgO); 5-1-7: $5Mg(OH)_2.MgSO_4.7H_2O$}.
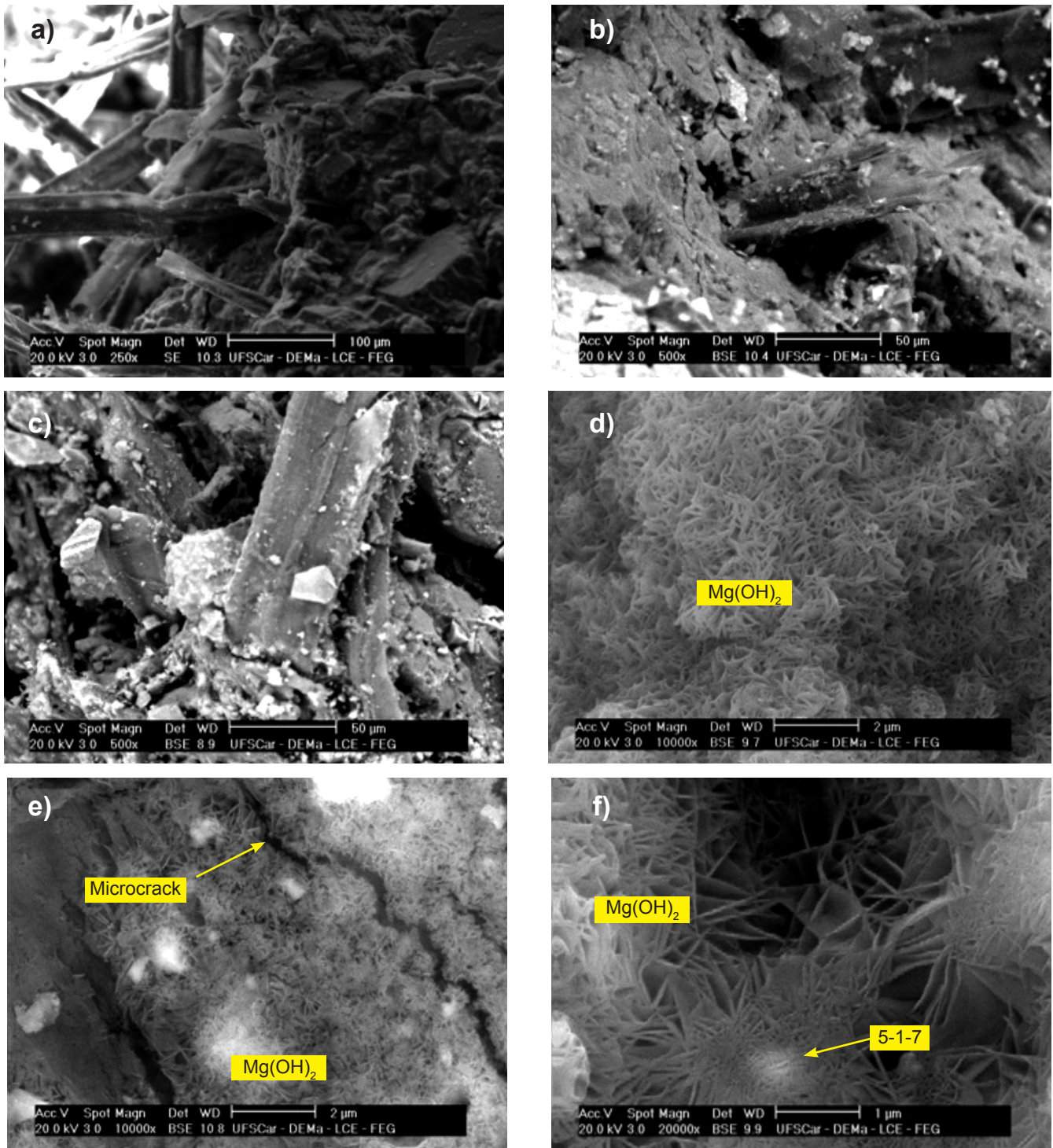
Figure 3: Scanning electron microscopy (SEM) images of carbonated and non-carbonated MOS-based fiber cement boards: a,b,d) non-carbonated reference sample (Ref); c) Carb24; e) Carb72; and f) Carb48.

CONCLUSIONS

The production of a cementitious composite with a magnesium oxysulfate (MOS) matrix reinforced with lignocellulosic fibers was achieved using the Hatschek process simulation. The material exhibited an average flexural strength (MOR) value close to 15 MPa after 7

days of curing. This property increased to approximately 18.5 MPa after the application of accelerated carbonation. Accelerated carbonation of the boards after different curing periods resulted in changes in the mechanical, physical, and microstructural properties of the produced materials. The carbonated materials after 24 and 48 h showed improved mechanical performance due to the formation

of carbonation products that increased the stiffness of the boards, resulting in increased material density when cured in a CO_2-rich atmosphere. However, the use of carbonation after 72 h led to a decrease in the mechanical strength of the materials. These observations were attributed to the potential reaction between the $5Mg(OH)_2.MgSO_4.7H_2O$ (5-1-7) phase (responsible for the mechanical strength of the materials) and CO_2 during carbonation reactions. The carbonation of this phase was confirmed by the reduction in the X-ray diffraction (XRD) peak related to the 5-1-7 phase when carbonation was performed after 72 h. The morphological analysis of the composite revealed the dispersion of the cellulose fibers in the inorganic matrix and good adhesion between the reinforcement and MOS cement. The accelerated carbonation process densified the material and formed carbonation products within the voids of the composite, which resulted in a decrease in water absorption by the boards. The presence of brucite $[Mg(OH)_2]$ and needle-shaped crystals (5-1-7 phase) was observed, confirming the XRD peaks found in the non-carbonated materials and the carbonated boards after different periods of carbonation.

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