

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

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## Abstract

In the search for unconventional binders that reduce energy consumption in production, magnesium oxysulfate (MOS) cement is an alternative. Besides that, the carbon dioxide (CO<sub>2</sub>) has been used to curing some products of MOS cement, for instance, magnesium fiber cement because this method improves their performance. The aim of this paper is to evaluate the effect of pre-curing before accelerated carbonation on the physical-mechanical changes of magnesium fiber cement boards. These boards were produced by the Hatschek process simulation and submitted a pre-curing of 24h, 48h and 72h after production. The correlation between microstructural changes and the physical-mechanical properties was observed by water absorption, apparent porosity, and apparent density, four-point bending test, X-ray diffraction and SEM analyses. The results demonstrated that pre-curing influenced the physical-mechanical properties of the produced boards. The carbonated materials after 72 hours showed a decrease in mechanical performance, which was attributed to the carbonation reactions between CO<sub>2</sub> and the hydration products responsible for the enhance of mechanical strength of the cementitious materials.

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

## INTRODUCTION

The development and rediscovery of alternative materials for the construction industry have seen significant growth in recent decades, such as magnesia-based cements. Brazil has been one of the world's leading producers of magnesite, the primary precursor to MgO, in recent years [1]. However, research on MgO-based construction materials is limited, necessitating further studies to enhance their application in the field.

Similar to the production of ordinary Portland cement (OPC) from limestone, magnesite is heated to produce MgO. Comparing the calcination temperatures of the processes, the calcination temperature of magnesite (approximately 750°C) is lower compared to the temperature used in OPC production (approximately 1450°C) to obtain reactive MgO, thereby reducing the energy consumption in the process [2,3]. However, the production of reactive MgO releases a significant amount of carbon dioxide (CO<sub>2</sub>) [4], which is particularly concerning due to the greenhouse effect of this type of gas [5], making it necessary to integrate carbon capture into the manufacturing process of MgO-based cements [6].

Magnesium oxysulfate cement (MOS) is a non-conventional binder produced through the reaction of magnesium oxide (MgO) and a magnesium sulfate (MgSO<sub>4</sub>) solution [7–9]. It offers advantages such as fire resistance, lightweight, low alkalinity, and low energy consumption, with lightweight panel production being its main application [10–12]. However, its instability under high humidity conditions, leading to reduced mechanical strength, has limited its insertion in the construction industry on a larger scale.

The mechanical properties of MOS cement depend mainly on the hydration reactions and the type and relative content of the hydration phase in the hardened cement. According to the ternary system of MgO-MgSO<sub>4</sub>-H<sub>2</sub>O, four oxysulfate phases are found at temperatures between 30°C and 120°C. I) 3Mg(OH)<sub>2</sub>-MgSO<sub>4</sub>-8H<sub>2</sub>O (3-1-8 phase), II) 5Mg(OH)<sub>2</sub>-MgSO<sub>4</sub>-3H<sub>2</sub>O (5-1-3 or 5-1-2 phase), III) Mg(OH)<sub>2</sub>-MgSO<sub>4</sub>-5H<sub>2</sub>O (1-1-5 phase) and IV) Mg(OH)<sub>2</sub>-2MgSO<sub>4</sub>-3H<sub>2</sub>O (1-2-3 phase) [13].

Considering that low mechanical and water resistance are among the major issues in the industrial applications of MOS cements, in 2005, Deng Dehua [14] reported a new hydration product produced with chemical additives that has the property of increasing the mechanical strengths and stability of the cement under high humidity conditions. Recently, Runcevski et al. [15] successfully analyzed the chemical composition and crystal structure of the new hydration product using modern techniques, discovering that a new MOS phase crystallizes with a stoichiometry of 5Mg(OH)<sub>2</sub>-MgSO<sub>4</sub>-7H<sub>2</sub>O (5-1-7 phase). The interwoven needle-like structure formed and its filling effect are the main reasons why the 5–1–7 phase improves the mechanical performance of cement [16,17].

The other alternative to enhance physical-mechanical performance of cementitious products is the accelerated carbonation. This process is a sequence of chemical reactions involving the diffusion of CO<sub>2</sub> through the saturated pores of a cement matrix [18]. To this end, the parameters used in the carbonation process such as CO<sub>2</sub> concentration, temperature, and humidity are factors that directly influence the speed and depth of

the progression of this phenomenon. Accelerated carbonation of MOS cements has been a limited study. However, in recent investigations, it was possible to improve the mechanical strength of the cement to some extent, in addition to reducing porosity and alkalinity, through carbonation [10], with these results it is possible to increase the durability of cellulosic fibers in this type of matrix. According to Qiyan Li et al. [19], integrating CO<sub>2</sub> capture during the curing of the pastes, improves the resistance to wetting-drying cycles. The results indicate that magnesium hydroxide and some basic magnesium oxysulfate phases are neutralized with carbon dioxide to form magnesium carbonate phases in MOS cement, which leads to structures with refined pores and an increase in mechanical strength.

According to the reduced energy consumption of MOS cement production [2,3], accelerated carbonation can be explored as the focus of the study is also directed to the benefits associated with environmental issues such as carbon capture [20].

The aim of this paper is to evaluate the effect of pre-curing (time before carbonation) on the physical-mechanical changes of magnesium fiber cement boards. According to experimental process, it was compared fiber-cement boards produced by the Hatschek process simulation without accelerated carbonation (reference) with boards pre-curing with accelerated carbonation after 24h, 48h and 72h of production.

## MATERIALS AND METHODS

### Materials

The MOS based fiber-cement boards were produced with a mixture of magnesium oxide powder (MgO), magnesium sulphate heptahydrate (MgSO<sub>4</sub>·7H<sub>2</sub>O), dolomitic limestone, citric acid and reinforced with unbleached eucalyptus cellulose fiber.

The MgO Q-MAG-200-AR (AR200), obtained by controlled calcination of magnesite (natural magnesium carbonate) and supplied by RHI-Magnesita S.A., Brumado, Bahia State, Brazil, it has a specific gravity of 3,45 g/cm<sup>3</sup> and surface area of 26,71 m<sup>2</sup>/g (SSA). Magnesium sulfate heptahydrate (commercial-grade Epsom salt, MgSO<sub>4</sub>·7H<sub>2</sub>O) was produced with a purity of 99,83%. The dolomite limestone was used as a filler in the fiber-cement boards, and it has density of 2,79 g/cm<sup>3</sup>. Citric acid of analytical purity was used in the mixture in a proportion of 0.50% in relation to the mass of MgO. The cellulose pulp used was obtained from unbleached eucalyptus paper kraft and were supplied by Suzano Papel e Celulose (Suzano, São Paulo State, Brazil).

### Sample preparation

The fiber cement boards were obtained from an adaptation industrial Hatschek process. The cellulose pulp was initially dispersed in a mixture of distilled water, MgSO<sub>4</sub> solution with a concentration of 25% and 0.50% of citric acid, at 3000 rpm for 5 min. Immediately afterwards MgO in a MgO:MgSO<sub>4</sub> molar ratio of 10 and dolomitic limestone at 10% of the amount of MgO by

mass (previously homogenized) were added, and the mixture was stirred for another 3 minutes. The paste was transferred to a perforated mould and a vacuum was applied. Subsequently, the board was pressed until it reaches a thickness of 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 hours. The boards were carbonated after 24, 48 and 72 hours of production. All samples were exposed to a concentrated CO<sub>2</sub> environment of 20% CO<sub>2</sub> and 60% relative humidity (RH) at 40°C for 6 hours to accelerate the carbonation process. It was used a climatic chamber with control of temperature, humidity and CO<sub>2</sub> concentration, Espec brand, model EPL-4H. The different samples produced by accelerated carbonation are presented in Table I.

Table I. Different samples produced by accelerated carbonation processes.

Sample	Period until start the accelerated carbonation process
Ref	Without carbonation
Carb24	24 hours
Carb48	48 hours
Carb72	72 hours

### Characterization of samples

The physical, mechanical, and microstructural characterization of the boards was performed 7 days after molding.

ASTM-C948-81 [21] was used to determine the physical properties. Water absorption (AA), apparent porosity (AP), and apparent density (AD) were the parameters that were examined.

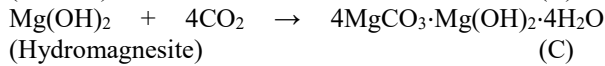
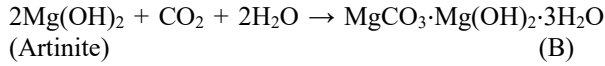
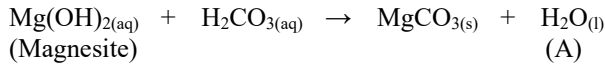
A four-point bending test [22] was performed on the boards to evaluate their mechanical properties. The test was performed using an EMIC DL30000 universal mechanical testing machine equipped with 5 kN loadcell and a deflectometer to detect the displacement in the center of the sample was used for the test. The modulus of rupture (MOR), limit of proportionality (LOP), modulus of elasticity (MOE), and specific energy (SE) were determined.

To identify phase evolution X-ray diffraction (XRD) and Scanning electron microscopy (SEM) were performed on samples extracted before and after of each different carbonation conditions. X-ray powder diffraction (XRD) pattern of fiber-cement boards was collected over a Horiba LA-60 diffractometer using CuK $\alpha$  radiation generated with a voltage of 40 kV and a tube current of 30 mA between 2 $\theta$  angles of 10-70°, 2°/min. The morphological analyses were performed using a microscopy Philips XL-30 FEG (Field Emission Gun).

## RESULTS AND DISCUSSION

The results of the mechanical tests for carbonated and non-carbonated fiber cement boards are presented in Table II. It is possible to observe that the carbonation

process caused changes in the properties of the materials produced. The carbonated boards, after 48 hours 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 hours 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<sub>2</sub> in the system. These reactions promote the formation of different magnesium carbonates, as shown in Equations A, B, and C.



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 increases its stiffness (increase in MOE) and consequently reduces the specific energy of the carbonated boards, as observed in Table II and modified the typical curves of stress *versus* flexural strain observed during the load test (Fig. 1).

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

Sample	MOR (MPa)	LOP (MPa)	MOE (GPa)	SE (KJ/m <sup>2</sup> )
Ref	15.16±1.63	12.40±1.95	9.89±1.24	3.44±0.48
Carb24	13.79±2.86	10.23±1.47	9.90±1.60	2.71±0.33
Carb48	18.47±0.95	14.66±0.90	10.52±1.37	2.93±0.70
Carb72	12.48±2.22	10.79±2.88	8.26±1.16	2.63±0.37

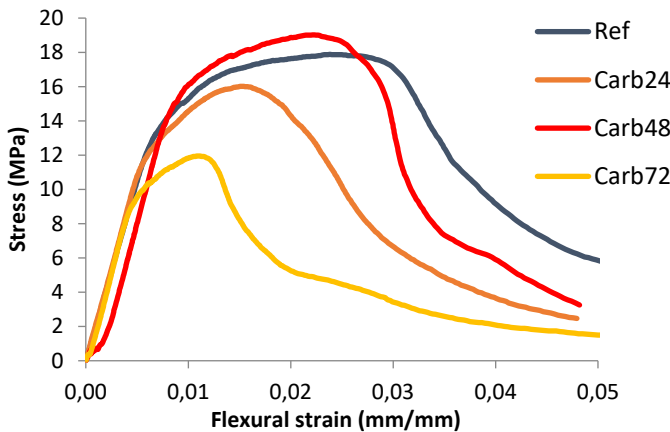


Figure 1: Typical bending test curves of the carbonated and non-carbonated boards.

Accelerated carbonation caused changes in the physical properties of the materials due to the formation of carbonates, as observed in Table III. The formation of these materials, 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 III. Physical properties of carbonated and non-carbonated boards.

Sample	Water Absorption (%)	Apparent porosity (%)	Bulk Density (g/cm <sup>3</sup> )
Ref	21.74±3.50	31.49±2.77	1.46±0.01
Carb24	18.08±1.76	27.59±1.78	1.53±0.05
Carb48	17.83±0.80	27.48±0.72	1.54±0.03
Carb72	20.67±1.22	29.47±2.50	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 Figure 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 [23,24]. It is 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 is observed. This decrease suggests that the carbonation process at ages beyond 72 hours favors 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 boards. Equation D represents the chemical process responsible for the consumption of the 5-1-7 phases (5-1-7 = 5Mg(OH)<sub>2</sub>.MgSO<sub>4</sub>.7H<sub>2</sub>O) during curing in a CO<sub>2</sub>-rich atmosphere.

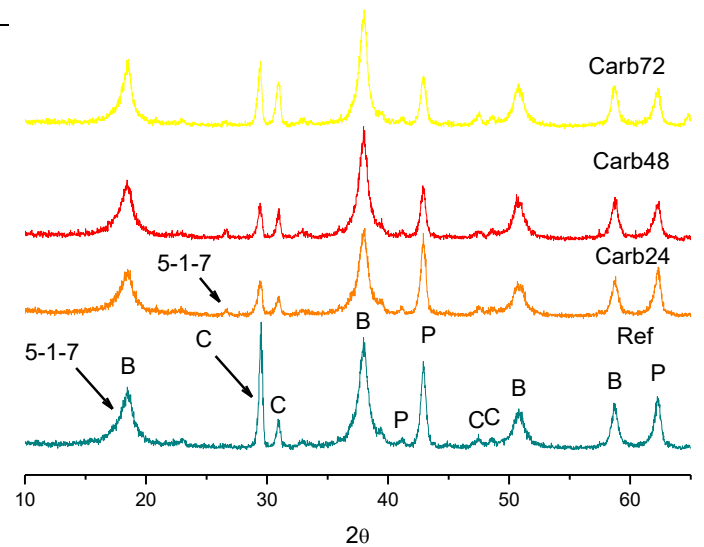
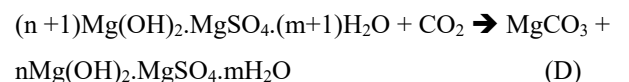


Figure 2: X-ray diffractograms of carbonated and non-carbonated MOS-based fiber cement samples. B - Mg(OH)<sub>2</sub>, C - CaCO<sub>3</sub>, P - Periclase (MgO) and 5-1-7 (5Mg(OH)<sub>2</sub>.MgSO<sub>4</sub>.7H<sub>2</sub>O).





After the accelerated carbonation process, the peaks corresponding to these phases disappear, 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.

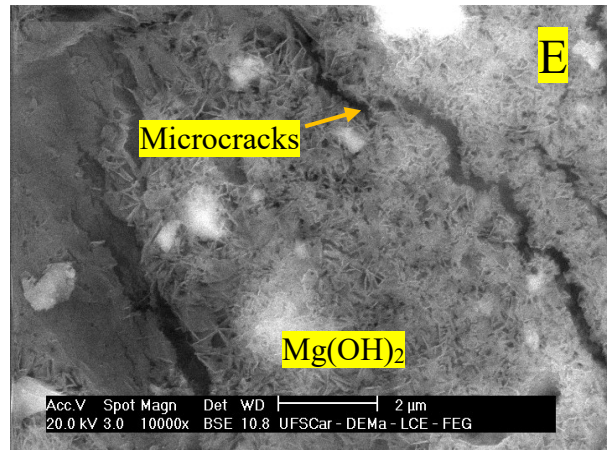
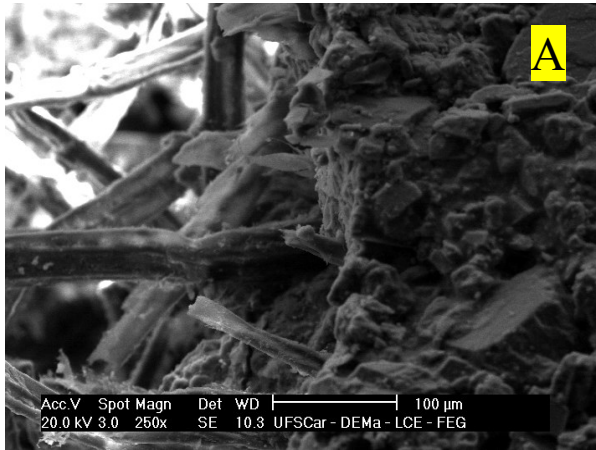


Figure 3: Scanning electron microscopy (SEM) images of carbonated and non-carbonated MOS-based fiber cement boards. (A), (B), and (D) represent the non-carbonated reference samples (Ref); (C) Carb24; (E) Carb72 and (F) Carb48.

The obtained images by scanning electron microscopy of the materials are presented in Fig. 3. It can be observed that the lignocellulosic reinforcement is dispersed within the material, which is related to the mechanical properties observed in the flexural tests. Fractured fibers were observed in the images (Figures 3A and 3B), indicating their adhesion to the inorganic matrix and subsequent fracture during mechanical loading. Figure 3B, it is possible to observe the presence of voids in regions close to the vegetal fibers. A reduction in the voids is observed in these regions after the accelerated carbonation process (Figure 3C). This

process occurs through the formation of hydration products, which promote a decrease in the void volume and water absorption of the composites. The presence of flake-like crystals was identified in all samples, which is associated with the formation of  $Mg(OH)_2$ , the main hydration product of MgO (Figure 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 samples after 72 hours (Carb72) exhibited a decrease in mechanical strength after curing in a  $CO_2$ -rich atmosphere. Morphological analysis of these samples revealed the presence of microcracks on the material surface (Figure 3E). These defects may be responsible for the reduced mechanical resistance observed in the Carb72 boards. The surface analysis of the Carb48 samples is presented in Figure 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 [25], 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.

## CONCLUSIONS

The production of cementitious composites with a magnesium oxysulfate (MOS) matrix and reinforced with lignocellulosic fibers was achieved using the Hatschek process simulation. The materials exhibited average flexural strength (MOR) values close to 15 MPa after 7 days of curing. These values 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 hours 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 hours led to a decrease in the mechanical strength values of the materials. These observations were attributed to the potential reaction between the 5-1-7 phases (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 diffraction peak related to the 5-1-7 phase when carbonation was performed after 72 hours. The morphological analysis of the composites 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 materials and formed carbonation products within the voids of the composites, which resulted in a decrease in water absorption by the boards. The presence of  $Mg(OH)_2$  brucite and needle-shaped crystals (5-1-7 phase) was observed, confirming the diffraction peaks found in the non-carbonated materials and the carbonated boards after different periods of carbonation.

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