The influence of carbonation on the performance of fiber cement reinforced with PVA fibers

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Abstract. The carbonation of cementitious composites can influence their properties, such as mechanical strength, porosity, drying shrinkage, etc. This paper aims at showing the effects of particle packing on the carbonation of fiber cement reinforced with PVA fibers. The experimental results compare the reference samples (Portland cement, limestone, cellulose, and PVA fibers) cured in environmental chamber (RH 90%, temperature at 23°C) with carbonated samples (5% CO\textsubscript{2}). The samples were produced in laboratory using vacuum filtration, which emulates a Hatschek process. Porosity, drying shrinkage, and MOR were measured by conventional methods. The results showed that the particle packing does not affect the carbonation significantly. The carbonation increases the shrinkage, and this may be attributed to the sum of drying and reduction of C-S-H phase by the carbonation chemical reactions. The carbonation also increases the mechanical properties of the fiber cement.

Introduction

The Hatschek process of fiber cement manufacture is complex and involves many production parameters. In the choice of raw materials, both the properties of the material and the process parameters must be considered, since there are many kinds of fillers that can be used in the fiber cement. In Brazil, it is common to use limestone as filler in the NT fiber cement\textsuperscript{1} composition in order to reduce the consumption of cement and control the rheological properties of the composite.

The particle packing factor that makes up the cementitious matrix is directly related to the porosity of the cured composite, so that various fiber cement properties are affected from this variable, such as the elastic modulus, mechanical strength, apparent density, drying shrinkage, and the speed of carbonation reactions. The use of different types of filler may modify the packing factor of particles, which results in differences in the porosity of the hardened material, and affects the diffusion of gas into the fiber cement, such as CO\textsubscript{2}.

The fiber cement sheet is a building material that can capture CO\textsubscript{2} from the environment during its lifetime. For example, for each 1 m\textsuperscript{2} of corrugated sheet tile with 6 mm thickness, it may be estimated that almost 3 kg of CO\textsubscript{2} are incorporated into the material (20% of cement mass). Factors such as high consumption of cement, high porosity, and high surface exposure \cite{1} are the causes of the very high amount of CO\textsubscript{2} incorporated. This aspect softens the CO\textsubscript{2} footprint associated with the production of this material.

The carbonation reaction has the favorable effect of CO\textsubscript{2} sequestration from the atmosphere, but it also modifies the properties of the fiber cement, such as increasing rigidity, reducing porosity, and...
providing greater dimensional stability. On the other hand, the differential carbonation shrinkage can cause great problems because it may favor the appearance of edge fissures [1].

The main point of this paper is to study how the addition of fillers of different sizes influences the porosity of the cementitious matrix of the fiber cement, and how this variation in porosity changes in the carbonation.

**Methodology**

The raw materials were characterized by means of laser particle size distribution test, surface area (BET), and density (Helium pycnometry).

The proportion of the raw materials used in the samples made in the laboratory is representative compared to fiber cement products industrially produced in Brazil, with 61.6% of cement, 33.5% of filler, and 4.9% of organic fibers (PVA and cellulose pulp). The samples were produced by the method suggested by Savastano [2], whose principle is the same involved in the Hatschek manufacturing process, which is filtering a reactive suspension followed by compression (compression pressure: 1 MPa) (Fig. 1).

![Fig. 1. Laboratory fiber cement production. Sequence: mixture, filtration, and compression.](image)

The porosity of the matrix phase is a variable of this study, and for that, 3 limestone fillers with different particle sizes were used in order to change the packing factor, and thus alter the porosity of the fiber cement.

After production, the samples were exposed to thermal curing for 24 hours (60 °C, RH> 90%), followed by wet curing for 9 days (23 °C, RH> 90%). After the curing period, the samples of the fiber cement were exposed to low relative humidity environment (50% RH) and temperature (23 °C) protected from exposure to CO₂. For this, soda lime was used, which captures the CO₂ in the air. Another part of the samples was exposed at room temperature and RH with identical conditions but with a high concentration of CO₂ (5%), in order to accelerate the carbonation reaction.

The isothermal calorimetry test was carried out in order to measure the effects of exposure to CO₂ on cement hydration kinetics. The same fiber cement samples were exposed to CO₂ after 30 minutes of the mixture with water. The changes in the heat of hydration were measured by isothermal calorimetry test performed at 30°C temperature, and the determination of changes in the hydrated compounds and carbonate formed by thermogravimetry.

The performance indicators of the effects of carbonation in fiber cement were the flexural performance tests, total porosity by Archimedes’ principle, and dimensional variation.

**Results**

**Materials characterization.** The materials used in this study were:

- Ordinary Portland Cement (OPC) → Portland cement type CPII F-32 (according to the Brazilian standard NBR 11578 [3]);
- Limestone Lim.3.1 → Calcite limestone with D₅₀ 3.1 μm;
- Limestone Lim.9.5 → Calcite limestone with D₅₀ 9.5 μm;
• Limestone Lim.16 → Calcite limestone with D$_{50}$ 16.0 µm;
• Cellulose pulp;
• PVA fiber.

The particle size distribution of the ground limestone fillers shows that a filler with particle size distribution similar to the OPC, another filler a little smaller than OPC, and a third filler 6 times smaller than OPC (Fig. 2.a) were used. Once the formulation was the same, the porosity of the fiber cement varied due to the size of fillers. The surface area presented a non-linear inverse correlation with the particle size (Table 1).

![Particle size distribution](image)

**Table 1. Density (γ) and surface area BET (S$_{BET}$).**

<table>
<thead>
<tr>
<th>Material</th>
<th>γ [g/cm³]</th>
<th>S$_{BET}$ [m²/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lim.3.1</td>
<td>2.759 ± 0.008</td>
<td>3.73</td>
</tr>
<tr>
<td>Lim.9.5</td>
<td>2.738 ± 0.011</td>
<td>1.16</td>
</tr>
<tr>
<td>Lim.16</td>
<td>2.762 ± 0.007</td>
<td>0.92</td>
</tr>
<tr>
<td>OPC</td>
<td>3.154 ± 0.027</td>
<td>1.59</td>
</tr>
</tbody>
</table>

Fig. 2. Particle size distribution of the (a) raw materials and the (b) cementitious matrix. The Andreasen q=0.37 curve indicates the maximum degree of particle packing (theoretical).

Since the constituent materials of fiber cement have different sizes, it is possible to design cementitious matrices with different packing rates of particles – volume actually occupied by the solid particles in relation to the total volume of the system [4]. When it has a structure with high packaging content, it means the existence of a small amount of voids, therefore a low porosity composite.

A particle packing degree indicator is the packing factor ($P_f$), which according to Funk and Dinger [5] can be defined as:

$$P_f = 1 - P_0$$  \hspace{1cm} (Eq. 1)

where $P_f$ is the packing factor and $P_0$ is the porosity.

The notorious Andreasen model of particle packing has a continuous approach and shows that the ideal particle packing is one in which, around two specific particles with very different sizes, there are similarity conditions [4]:

$$CPFT = \left(\frac{D_P}{D_L}\right)^q \times 100$$  \hspace{1cm} (Eq. 2)
where CPFT is the cumulative percentage of particles smaller than \( D_P \); \( D_P \) is the particle diameter; \( D_L \) is the diameter of the largest particle and \( q \) is the distribution coefficient. Computer simulations have shown that a value of \( q = 0.37 \) is what provides the maximum packing density [5], [6]. Fig. 2.b shows that the matrix that utilizes limestone Lim.16 has a deficit of particles smaller than 20 µm. While using a smaller-sized filler, this smaller particle debility is suppressed. For the Matrix.Lim.3.1, this deficiency occurs for particles smaller than 5.5 µm.

The packaging project in composites reinforced with fibers must consider the problems caused by the fibers, also contributing with the appearance of more voids. The porosity of the resulting fiber-fiber and fiber-matrix interactions is due to the formation of a structural arrangement of the fibers and the wall effect provided by the asymmetry, size, and spatial arrangement of the fiber in the matrix [4].

When the fiber is short enough to stay in the created voids between the particles, this can contribute to the packaging of the suspension, without creating any disturbance in the packaging factor [7]. In the case of fiber cement, where the PVA fibers have a length greater than the gap created between the particles (length: 6 mm, diameter: 16 µm), the porosity may occur due to contact of the particle surface with the fiber surface.

There is a region with greater porosity around the fiber due to the wall effect [7], and it is characterized by a disorder volume whose size is proportional to the particle size and fiber length. The packaging disturbing effect is reduced when the fibers are flexible. However, when considering the small solid particles as much as the flexibility of the fiber, a contact between the extensive surface area of the fiber and the small surface area of the grains will happen, representing the wall effect.

The fillers used are calcite nature, according to the results of thermogravimetric analysis, with amount of CaCO\(_3\) higher than 91%. The Portland cement used has the addition of 7.55% of limestone, 4.42% loss on heat, and its chemical composition is shown in Table 2.

<table>
<thead>
<tr>
<th>SiO(_2)</th>
<th>Al(_2)O(_3)</th>
<th>Fe(_2)O(_3)</th>
<th>CaO</th>
<th>MgO</th>
<th>SO(_3)</th>
<th>Na(_2)O</th>
<th>K(_2)O</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC</td>
<td>18.7</td>
<td>4.13</td>
<td>2.85</td>
<td>64.5</td>
<td>5.44</td>
<td>2.10</td>
<td>0.11</td>
</tr>
</tbody>
</table>

**Table 2.** Chemical composition by XRF – X-ray fluorescence [%].

**Hydration kinetics.** The carbonation of cementitious composites is a widely studied topic. Carbonation is a decalcification process in which the portlandite and C-S-H lose calcium in their composition. Carbonation chemical reactions occur in the already hydrated cement matrix. The main product of the interaction between CO\(_2\) and portlandite is calcium carbonate [8]. The main product of the interaction between C-S-H and CO\(_2\) is the decalcification of C-S-H (decreased of the Ca/Si ratio) with shrinkage when Ca/Si ratio is less than 1.2 [9].

![Fig. 3 Isothermal calorimetry results.](image-url)
The early exposure in an environment with high concentration of CO₂ can modify the hydration kinetics of the cement matrix, altering the velocity of the chemical reactions, the hydrated compounds and formed carbonates, and the short-term properties of the materials. The hydration kinetics of fiber cement matrix is represented by the generated heat flow during the hydration time. After 30 minutes of added water, the CO₂ exposure altered the hydration kinetics of the cementitious matrix, as shown in Fig. 3.

CO₂ was inserted in the testing capsule after 30 minutes of added water, at the same testing temperature (30°C). The thermic equilibrium of the gas inside the capsule has generated a small energy peak that reached -0.00015 mW/g. The first 45 minutes of the experiment suffered interference from the thermic equilibrium between the mass of the sample and the capsule of the calorimeter. However, it is possible to observe that CO₂ reacts with the suspension immediately after the exposure, generating a lot of heat (heat flow peak: 63 mW per gram of cement; accumulated heat: 62.62 J per gram of cement).

The exposure to CO₂ has accelerated the starting of the precipitation of C-S-H (acceleration period) in 30 minutes. However, the accumulated heat during this period was 4.98 J/g less in comparison with the reference sample. The accumulated heat during the precipitation of ettringite and monosulfoaluminate was also smaller in the carbonated sample, in this case 12.85 J/g in comparison with the reference sample.

The TG – thermogravimetry – results showed that the biggest difference between the carbonated samples happened at the thermal decomposing temperature range between 230 e 300°C, due to the water loss of the mono (3CaO·Al₂O₃·CaCO₃·11H₂O) [8] and the hemi-carboaluminate (3CaO·Al₂O₃·0.5Ca(OH)₂·0.5CaCO₃·11.5H₂O) [10]. These results show that the first product formed by the carbonation reaction resulted from the interaction between the hydrate aluminates (hydrogarnet phase) with CO₂. During the hydration time t₁ (after the induction period), there was a small increase in volatile loss of 1.4% from the formation of 4.02% of monocarboaluminate. After 700°C, the carboaluminate loses a fraction of combined CO₂. At time t₂ (after the acceleration period – rapid C-S-H and portlandite formation), the same behavior was observed, with an increase of 2.07% in the volatile amount on the carbonated sample, which is equivalent to the formation of 5.94g of monocarboaluminate, per 100 grams of fiber cement.

The differences between the curves t₁ and t₂ result only in the difference on the hydration degree, with the formation of C-S-H, measured by the mass loss after 70°C, which can go up to 500°C [11]; and the formation of portlandite, measured by the mass loss when reaching 450°C (reference sample: 7.40g of portlandite per gram of fiber cement) (Fig. 4).

![Fig. 4. TG and DTG curves of fiber cement carbonated (CARB) and non-carbonated (REF), (T1) after the induction period and (T2) after the acceleration period (rapid C-S-H and portlandite formation by C₅S).](image-url)
The chemical reactions involved in the conventional carbonating process, which occur in the hydrated sample of cement, start with the reaction of CO$_2$ with cement pore water, forming carbonic acid, which reacts with calcium hydroxide, then forming calcium bicarbonate, and finally calcium carbonate. In spite of that, alterations were not observed in the amounts of calcium carbonate in the carbonated samples, since the main change measured was the formation of carboaluminate from the first hydrated aluminates. Due to the short duration of the chemical reactions, the hydration degree of carbonation is small.

**Porosity.** The particle packing concept is defined by the adequacy of material proportion in different granulometries, so that the bigger voids may be filled with smaller particles, which will have their voids filled with even smaller particles, and so on [4]. By using limestone Lim.16, it is possible to replace reactive particles (OPC) by inert particles (Lim.16) of the same size, and by doing so, one can observe the effect on the reactive phase on the carbonation. When using the limestone sample Lim.3.1, whose size of the particles is smaller than the cement, it is expected an increase in the particle packing, and therefore, porosity decrease.

The porosity of the fiber cement samples was determined by Archimedes’ principle through measurements of the dry, saturated, and immersed mass of samples (Eq. 3).

\[
P = \frac{m_{\text{sat}} - m_{\text{dry}}}{m_{\text{sat}} - m_{\text{im}}}
\]

(Eq. 3)

One sample of fiber cement with cementitious matrix composed by only cement was used as reference (FC.ref). The samples containing limestone showed bigger porosity (Fig. 5) once there is smaller volume formation of the hydrated compounds, with the exception of the sample containing limestone Lim.3.1 (FC.3.1) because of better particle packing.

![Fig. 5. Total porosity.](image)

The carbonation reactions reduced the porosity of the fiber cement. It occurs due to the formation of calcium carbonate from the added CO$_2$, which occurs in the pores of the fiber cement. Once the carbonation is a chemical reaction that happens in cement hydrated compounds, the bigger amount of cement in the formulation results in bigger effects observed in the porosity, as shown in sample FC.ref. In spite of the porosity of the non-carbonated sample FC.ref and FC.3.1 being equal between them, the reduction of the porosity was smaller in the sample with limestone due to the lower fraction of cement content in its formulation.
Rheological properties. The use of different types of filler can change the rheological behavior of the fiber cement, which affects the manufacturing process. The differences in the rheological properties can affect, for example, the particle retention in the Sieve Cylinder, the compression efficiency of the fresh fiber cement, the fresh humidity, molding the corrugated sheets, etc. These differences affect the performances of the cured fiber cement, e.g. in the crack occurrence, material density, mechanical performance, permeability of the tiles, etc.

During the compression of the samples produced in laboratory, a load of 1 MPa was applied to the filtered sample. During this compression step, the squeeze-flow test was performed, which measured the compressive deflection to the same compressive load.

The squeeze-flow results presented that the fiber cement sample FC.ref showed less resistance to the applied load (higher deformation) (Fig. 6), indicating less consistency. The greater superficial area demands larger quantity of water for wetting, which consequently facilitates the flow of the particles (less shear stress). The sample with the smaller limestone (FC.3.1) showed less consistency between the samples with limestone because it has the greatest superficial area.

Samples FC.9.5 and FC.16 showed high resistance to the applied load (less deformation). Sample FC.9.5 is the one that presents the worst packing between the particles, impairing the flow, and therefore it showed a higher lower compressive extension (Fig. 6).

![Squeeze-flow results](image)

Shrinkage. Hygroscopic movement, carbonation, and chemical shrinkage occurred in the hydrated cement compounds. These are the three factors that can promote shrinkage in cementitious materials. The fiber cement favors these factors due to their high porosity (large hygroscopic movement and ease of diffusion of CO\textsubscript{2}) and large cement content (favors carbonation and chemical shrinkage).

The total porosity of commercial air-cured fiber cement ranges from 30% to 45%, which is of the same magnitude as mortars (ranging from 30% to 50% [12]), and significantly more than concrete, which is approximately 15% [13]. Furthermore, the pore size distribution favors an increase in the capillary pressure and thus contributes to shrinkage.

Fig. 7 shows the pore size distribution of a typical NT fiber cement sample. Clearly, the profile can vary due to several factors such as formulation, raw materials, and curing. Capillary pressure only occurs in the capillary pores (diameter between 0.01 and 10 micrometers) [14], being higher in mesopores (Fig. 7-II) and lower in macropores (Fig. 7-III). Out of the total porosity of 35%, approximately 30% is from mesopores and macropores. Thus, we can estimate that macropores cause approximately 50% of the total drying shrinkage of the cement.
Carbonation involves the diffusion of carbon dioxide into the material. Fiber cement sheets are thin and have large surface areas. They also are highly porous. These two aspects allow for fast drying and diffusion of CO$_2$. The CO$_2$ will react with hydrated products, mainly calcium hydroxide, resulting in changes in porosity, water loss, and shrinkage. Because the volume fraction of the cement paste in the fiber cement is much higher than in the concrete, shrinkage due to carbonation is higher too. In just 14 days of exposure to an environment of 5% carbon dioxide, dry fiber cement will shrink approximately 2.2 mm/m, with formation of 18.2 g of CaCO$_3$ per 100 g of cement [15].

The drying shrinkage results showed no major differences between the samples (Fig. 8). The FC.ref sample has higher volumetric variation. This behavior occurred due to the amount of cement, which increased the refinement of the pores (smaller pores). Once the drying shrinkage has the capillary pressure that occurs during drying as a principle, the pore size affects the shrinking magnitude.

Comparing the samples containing limestone, the sample with less total porosity has smaller shrinkage. The relationship between shrinkage and mass loss shows susceptibility to shrinkage of the composite, i.e. it indicates what the amount of drying shrinkage is for the same mass loss. Fig. 9 shows that the larger amount of cement makes the fiber cement more susceptible to shrinkage (the trend line slope of the FC.ref sample is greater than the slope of the other limestone samples).
The carbonation results in the shrinkage of the fiber cement due to the greater density of the C-S-H molecule, in which these molecules become longer, but denser, resulting in a smaller total volume. The carbonation shrinkage has almost the same magnitude of the drying shrinkage, as shown in Fig. 8, in which the samples that had suffered carbonation and drying simultaneously presented shrinkage up to 2 times larger than the samples that only dried.

The drying shrinkage is a function of the matrix pore size distribution. However, the carbonate shrinkage is a function of the amount of reactive phases with CO$_2$ present in the sample, i.e. the amount of cement. For this reason, the total shrinkage was higher in FC.ref sample (Fig. 8).

**Flexure resistance.** The mechanical performance of the fiber cement was measured by the flexural strength test. From this test, it was determined the modulus of rupture (MOR) and the limit of proportionality (LOP), which is the maximum load of the elastic period.

\[
MOR = \frac{P_{\text{max}}\cdot L}{b\cdot e^2} \tag{Eq. 4}
\]

\[
LOP = \frac{P_{\text{lop}}\cdot L}{b\cdot e^2} \tag{Eq. 5}
\]

where: P – test load [N]; L – distance between the supports (135 mm); b – width of the sample [mm]; and thickness of the sample [mm].

The limestone size influenced the flexural strength of the fiber cement. The resistance of the samples with limestone was of the same magnitude of the FC.ref sample (Fig. 10), even though the cement content in these samples was lower (61.6%) than the reference sample (95.1%). The finest limestone (Lim.3.1) resulted in a fiber cement with greater MOR due to better packing of particles.

The carbonation increased flexural resistance. The LOP increased almost twice, and the MOR also increased significantly. The carbonation changes the properties of the matrix, improving its rigidity and resistance, but the fiber cement deformation capacity decreases.
Fig. 10. Flexure performance. Typical curves (eight specimens were tested per formulation).

Conclusions. We demonstrate that is possible to use the packing particle as strategy for controlling the properties of fiber cement.

The limestone does not influence the cement hydration. However, it is possible to improve the performance of the fiber cement with this type of filler. It is also possible to improve the particle packing with filler smaller than cement, and consequently improve the mechanical strength.

The use of filler reduces the drying shrinkage susceptibility, and this is a very good aspect because it prevents the cracking, especially on the edge. It is possible to reduce the total porosity with an optimized packing project, resulting in a low total drying shrinkage.

Another strategy to improve the performance of the fiber cement is carbonation. The results showed that carbonation significantly improves the flexural performance. Once the particle packing factor influences the carbonation, it is possible to improve the carbonation effects with the correct filler.

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References


