

Article

A Novel Method for Calcium Carbonate Deposition in Wood That Increases Carbon Dioxide Concentration and Fire Resistance

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Abstract: In this study, a novel method for calcium carbonate deposition in wood that increases carbon dioxide concentration and fire resistance is proposed. The method promoted the mineralization of radiata pine wood microstructure with calcium carbonate by using a process consisting in the vacuum impregnation of wood with a calcium chloride aqueous solution and the subsequent sequential diffusion of gaseous ammonium and carbon dioxide. In the most favorable conditions, the method yielded a weight gain of about 20 wt.% due to mineralization, which implied the accumulation of 0.467 mmol·g⁻¹ of carbon dioxide in the microstructure of wood. In addition, a weight gain of about 8% was sufficient to provide fire resistance to a level similar to that achieved by a commercially available fire-retardant treatment. The feasibility of retaining carbon dioxide directly inside the wood microstructure can be advantageous for developing wood products with enhanced environmental characteristics. This method can be a potential alternative for users seeking materials that could be effective at supporting a full sustainable development.

Keywords: carbon dioxide accumulation; wood fire-protection; calcium carbonate; in situ mineralization; wood protection



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1. Introduction

The increasing interest in wood as a building material is driven by its outstanding physical and mechanical behavior and versatility, but also by its biodegradable nature and ability to act as a carbon reservoir [1]. For these characteristics, many final users, seeking materials supporting sustainable development, have turned their attention to wood and wood products [2]. The use of wood in construction ensures that an important portion of the carbon incorporated by trees during their growth will remain sequestered in wood fibers for a long time [3]. Unfortunately, wood's ability to act as a carbon reservoir ends when it is degraded, and carbon is released to the atmosphere [4]. Among the agents of deterioration, fire stands out because of its devastating effects, which can almost wholly degrade wood cells in a very short time. Thus, fire is a significant risk in any construction containing wooden elements.

Fire retardancy in wood products is regularly achieved by superficial or integral impregnation with chemical formulations. In this sense, a wide range of very effective formulations, mostly based on the action of phosphorus, nitrogen, and boron compounds, have been developed [5]. However, nowadays many of these formulations have been questioned because of their possible toxic effects on living organisms [6–8]. For instance,

the release of chlorinated and brominated dioxins and dibenzofurans during accidental fires or waste incineration is a recurrent concern [8]. Consequently, the development of new and innovative technologies for wood's fire protection, capable of meeting the current environmental demands, is an evident necessity.

Mineralization treatments can certainly be accounted as an option to protect wood against fire while reducing the risk of releasing toxic compounds during its thermal degradation. Examples of innovations in such area can be found in the development of treatments promoting an accelerated petrification of wood [9,10] and others based on the formation of a wide range of minerals with inherent fire resistance properties inside the wood cells [11,12]. Several authors have proposed calcium carbonate (CaCO_3) as a fire protection agent for wood products [13–16]. During the endothermic decomposition of CaCO_3 , the release of carbon dioxide (CO_2) apparently dilutes and cools combustion gases, reducing the effectiveness of the combustion [14]. The thermal degradation of CaCO_3 does not generate toxic compounds and therefore is considered an environmentally friendly treatment [14,17–19]. Cone calorimetry tests on wood treated with CaCO_3 have shown up to a 65% decrease in heat release capacity, demonstrating the great potential of the treatment. In addition, the intrinsic properties of wood are not significantly affected, expanding its reliability in construction uses [14,17].

In this work, we synthesized CaCO_3 inside the microstructure of radiata pine samples using a novel process that consisted in vacuum impregnation of an aqueous solution of calcium chloride (CaCl_2) and subsequent sequential diffusion of gaseous ammonium (NH_3) and CO_2 . The main objective of the study was to verify the feasibility of an innovative treatment to accumulate CO_2 inside wood that simultaneously could improve the response of wood against the action of fire, as the CO_2 involved in the reaction becomes part of the salt crystals of CaCO_3 accumulated in the wood microstructure. Specifically, we planned to verify the level of fire protection offered by the best conditions of the treatment, if any, and the amount of CO_2 accumulated inside the wood in such conditions.

2. Materials and Methods

2.1. Wood Samples

Radiata pine (*Pinus radiata* D. Don) wood pieces, acquired at a local lumber store, were used to prepare two sets of samples. The first set consisted of cubic sapwood pieces with perfectly tangential, radial, and transverse faces (20 mm \times 20 mm \times 20 mm). The second set consisted of 6 mm \times 150 mm \times 300 mm wood pieces with the tangential section on the main face and the end grain oriented along the longest axis. These samples were not screened for the presence of sapwood or heartwood. All samples were dried to anhydrous conditions in a convection oven at 50 °C, and their anhydrous mass was recorded. After that, the samples were conditioned at 65% relative humidity (R.H.) and 21 °C for two weeks, prior to the impregnation treatment.

2.2. Mineralization Treatment

CaCO_3 accumulation inside the wood microstructure was conducted on the 20 \times 20 \times 20 mm ($n = 100$) conditioned samples. The samples were vacuum-impregnated (−1 atm, 120 min) with CaCl_2 (7.5%, 15%, 30%, and 60% w/v) in a stainless-steel vessel (30 L, approx.). After that, the samples were removed and then sequentially exposed to gaseous ammonia (40 °C for 60 min, atmospheric pressure) inside a vaporizing chamber and to CO_2 (99%, 60 min, 4 bars, room temperature) inside the stainless-steel vessel. The aim of using gaseous ammonia was to promote a rapid change of pH throughout the wood section, creating an alkaline environment, in which the presence of CO_2 could initiate the reaction of mineralization of CaCl_2 into CaCO_3 . Similarly, the use of gaseous CO_2 was expected to improve the penetration of the mineralization treatment. After the treatment, the samples were washed overnight in distilled water at neutral pH to remove residual salts and byproducts. The whole process was consecutively repeated, producing cycles of treatment from 1 to 5. The treated samples were oven-dried at 50 °C until constant weight

(± 0.002 g), and the anhydrous mass was recorded and afterwards used to calculate the weight gain of the treatment according to Equation (1):

$$\text{Weight gain (\%)} = [(m_2 - m_1)/m_1] \times 100 \quad (1)$$

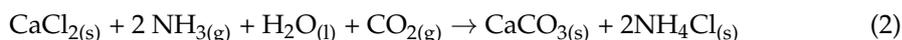
where m_1 and m_2 are the anhydrous mass of the samples before and after the mineralization treatment, respectively.

2.3. Scanning Electron Microscopy and Energy-Dispersive X-ray Spectroscopy

Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) analyses were used to observe the accumulation of salt crystals inside the wood microstructure and assess their chemical composition. SEM and EDS evaluations were performed on samples that achieved the higher weight gains. Primarily, observations were made at the surface and then at 5 and 10 mm depth, using a JEOL-JSM 6380 (Tokyo, Japan) scanning electron microscope and an acceleration voltage of 20 kV.

2.4. Carbon Dioxide Accumulation Due to the Mineralization Treatment

The concentration of CO_2 accumulated inside the wood microstructure due to the mineralization treatment was indirectly determined by assessing the gain of calcium in the samples. According to the chemical reaction associated with the mineralization treatment, each molecule of calcium acquired by the wood due to the accumulation of CaCO_3 reacted with one molecule of CO_2 (Equation (2)). Thus, for each mol of calcium accumulated in the wood, at least one mol of CO_2 was captured due to the treatment.



Calcium concentration in the samples was measured by Atomic Absorption Spectroscopy (AAS) by using $20 \text{ mm} \times 20 \text{ mm} \times 40 \text{ mm}$ wood samples ($n = 5$). These samples were sawn in half to obtain 10 paired samples of $20 \text{ mm} \times 20 \text{ mm} \times 20 \text{ mm}$. Five of the paired samples remained as controls without treatment, and the other five were mineralized until reaching a 20% weight gain. After treatment, the samples were grounded in a small grinder to 200 mesh, and then the ash content was determined according to ASTM 1755-01(2020). The grounded samples were digested using a mixture of 18 mL HNO_3 and 7 mL HCl (final volume 25 mL). The samples were boiled for 2 h in covered beakers on a hot plate. Then, the digested samples were transferred and diluted to 100 mL with distilled water. The resultant products were measured and analyzed in an iCE 3000 Series Atomic Absorption Spectrometer (Thermo Fisher Scientific, Waltham, MA, USA). The initial content of calcium in the samples was subtracted from the content of calcium measured after the mineralization treatment. This information was used to calculate the mol of calcium per gram of anhydrous wood and hence the content of CO_2 .

2.5. Infrared and Thermogravimetric Analyses

The Fourier transform infrared spectroscopy (FTIR) spectra of the untreated and mineralized samples, as well as of the pure CaCO_3 standard, were measured by direct transmittance using the KBr pellet technique. The spectra were recorded in the range of $4000\text{--}400 \text{ cm}^{-1}$ using a Thermo-Nicolet Nexus 670 FTIR (Thermo Fischer Scientific, Waltham, MA, USA). Pretreatment was carried out by grinding the samples in a mill to 200 mesh and, subsequently, by compressing the mixture of each sample and KBr (where KBr has a ratio of 0.5 wt.%–1 wt.%).

In addition, 2.5 mg of each grinded sample was used to conduct a thermogravimetric analysis (TGA) in a TG 209F3 Tarsus from NETZSCH Instruments (Selb, Germany) thermogravimetric analyzer. These tests were conducted in an ultra-high purity nitrogen atmosphere with a heating rate of $20 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$, from 50 to $600 \text{ }^\circ\text{C}$. The weight loss relative to the temperature values was used to perform the derivative thermogravimetric analysis (DTG). All TGA tests were performed in triplicate.

2.6. Fire Resistance Test

The fire resistance of the wood samples was tested according to Chilean Standard NCh1974 (Figure 1). The samples were ignited in controlled conditions inside a 400 mm × 700 mm × 810 mm cabinet, under a constant air flux ($0.2 \text{ m}\cdot\text{s}^{-1}$). In the test, the samples are individually placed in the middle of the cabinet laying at 45° . Then, in a stainless-steel container, a known volume of absolute ethanol is burned directly under the samples. The test lasts until the total combustion of the fuel is achieved and the flames in the sample are completely off.



Figure 1. Fire resistance test according to the Chilean Standard NCh1974. The samples are ignited inside a 400 mm × 700 mm × 810 mm cabinet under a constant air flux ($0.2 \text{ m}\cdot\text{s}^{-1}$). Blurriness of the image due to the template glass cover on the front of the cabinet.

Wood samples, 6 mm × 150 mm × 300 mm ($n = 15$), were mineralized using the conditions that resulted in the highest accumulation of calcium carbonate, treated with the commercial fire-retardant agent AF7000 (AF7000 Fire Protection, Industrial y Comercial Ciprés Ltda, Santiago, Chile), or left without treatment to act as control samples. The fire-retardant agent was selected due to its commercial availability and chemical composition based on boric and phosphoric acid and ammonium sulfate [20]. The fire-retardant agent was applied by brushing, according to the manufacturer's instructions, on samples previously conditioned at 65% R.H. and 21 °C for 2 weeks.

Before the combustion test, all samples were oven-dried at 50 °C until constant weight ($\pm 0.002 \text{ g}$), and their mass recorded. After the combustion, the samples were allowed to cool down, and their mass was recorded again and used to calculate the weight loss due to combustion (Equation (3)). In addition, the maximum extension of the carbonization in each axis of the samples was recorded in mm and used to calculate the carbonization index according to Equation (4).

$$\text{Weight loss} = [(m_1 - m_2)/m_1] \times 100 \quad (3)$$

where m_1 and m_2 are the mass of the samples before and after the combustion, respectively.

$$\text{Carbonization index} = L_1 \times L_2 \times L_3 \quad (4)$$

where L_1 , L_2 , and L_3 are the maximum extension of the carbonization at the length, width, and depth of the sample, respectively.

2.7. Data Analysis

Analysis of variance (ANOVA) was used to evaluate the mineralization and fire resistance of the wood samples. The mineralization experiment was conducted according to a factorial design that tested the concentration of CaCl_2 and the number of cycles of treatment as factors, while the weight gain of the samples after treatment was considered as the main response. Similarly, ANOVA was used to test the effect of the fire-retardant treatment on the wood samples. Such analysis considered as responses the weight loss due to combustion and the carbonization index. In all cases, after ANOVA ($p < 0.05$), significant differences were estimated using Fisher's least significant test (l.s.d.) and expressed as error bars in the different result charts.

Statistical analyses were performed using the Software Design-Expert 11 (Stat-ease, Inc., Minneapolis, MN, USA, version 11).

3. Results

3.1. Mineralization Treatment

The results of the mineralization experiments are depicted in Figure 2. The ANOVA results, available as Supplementary Data (Figure S1), indicated a significant effect (p -value < 0.05) of CaCl_2 concentration, the number of treatment cycles, and the interaction of these two factors. Figure 2 shows that the increment of the treatment cycles had a significant effect only until the fourth cycle. Similarly, 30% CaCl_2 concentration yielded significantly higher weight gains values compared to other concentrations. Nevertheless, relevant interactions detected among factors showed that the highest weight gain, 22% in samples treated with five cycles using CaCl_2 at a concentration of 30%, was not significantly different than those obtained in samples treated with five cycles; 15% CaCl_2 , and 4 cycles; 15% and 30% CaCl_2 . With the goal to establish adequate conditions for the treatment of larger samples, four cycles and 30% CaCl_2 were chosen as treatment conditions to mineralize the fire-resistant test samples.

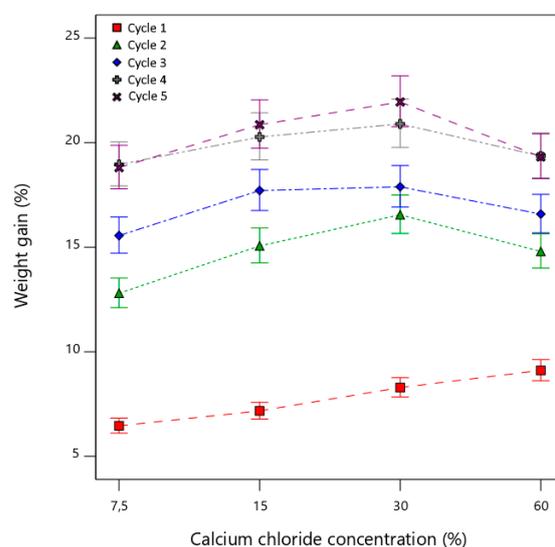


Figure 2. Weight gain of radiata pine samples mineralized for calcium carbonate accumulation. Error bars depict the least significant difference (l.s.d.) after analysis of variance ($p < 0.05$).

SEM images of samples treated with 30% CaCl_2 , five cycles, show that the treatment induced an extended mineralization of the external area of the samples (Figure 3). Mineralization was less prevalent at 5 mm depth, forming semispherical particles, and apparently absent at 10 mm depth. EDS analysis of the samples showed that the amount of calcium present at the surface of the observed samples was 35.6% (Figure 3a). This amount decreased to 3.6% at 5 mm depth and to 1.08% at 10 mm depth (Figure 3b,c), which was almost equal to that measured in an untreated sample. The EDS analysis of the semispherical

particles found in the interior and at the surface of the samples (Figure 3d) and at 5 and 10 mm depth in the treated samples was stoichiometrically sufficient to determine CaCO_3 presence. This clearly contrasts with the results obtained for the untreated surface, where the content of C, O, and Ca were 52.85%, 46.39%, and 0.79%, respectively.

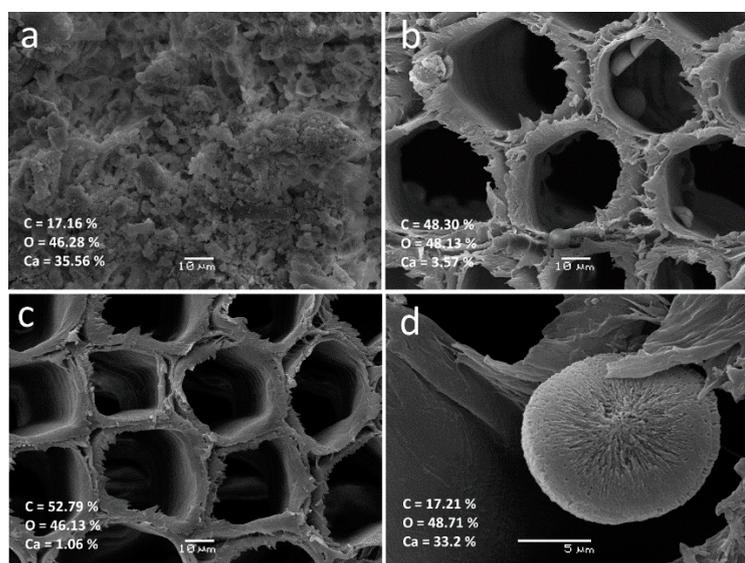


Figure 3. SEM images of a sample treated with 30% calcium chloride, five cycles. (a) Surface of the sample; EDS chemical determination: C = 17.16%, O = 46.28%, and Ca = 36.56%, bar size 10 μm ; (b) 5 mm depth from the surface of the sample; EDS chemical determination: C = 48.30%, O = 48.13%, and Ca = 3.57%, bar size 10 μm ; (c) 10 mm depth from the surface of the sample; EDS chemical determination: C = 52.79%, O = 46.13%, and Ca = 1.06%, bar size 10 μm ; (d) semispherical particle formed due to the mineralization process; EDS chemical determination: C = 17.21%, O = 48.71%, and Ca = 33.2%, bar size 5 μm .

3.2. CO_2 Concentration

The gains of weight, calcium, and CO_2 , of selected wood samples are shown in Table 1. The average carbon dioxide gain was 0.467 ($\text{mmol of CO}_2 \cdot \text{g}^{-1}$ of anhydrous wood) for samples that achieved about 20% weight gain (wt.%) due to the mineralization treatment. These samples were treated with an initial CaCl_2 concentration of 30% in four consecutive cycles.

Table 1. Gains of weight, calcium, and carbon dioxide in mineralized samples.

Sample	Weight Gain (%)	Calcium Gain (%)	CO_2 Gain ($\text{m} \cdot \text{mol} \cdot \text{g}^{-1}$ Anhydrous Wood)
1	20.40	1.55	0.490
2	20.50	1.96	0.602
3	19.01	1.19	0.381
4	20.20	1.56	0.489
5	20.10	1.15	0.374

3.3. Infrared Analysis

The FTIR spectrum of pure CaCO_3 showed the presence of a strong band centered around 1453 cm^{-1} , characteristic of the C–O stretching mode of carbonate, together with a narrow band around 873 cm^{-1} characteristic of the bending mode (Figure 4B). These bands were also observed in the CaCO_3 -treated wood sample, showing an increased absorbance in both wavenumbers (Figure 4A). Additionally, when both spectra were compared, it was observed that the treated wood sample showed differences at 1050 cm^{-1} that corresponded

to C=C stretching vibrations in the aromatic structure. Interestingly, a variation was seen at 1735 cm^{-1} associated with the stretching vibrations of unconjugated C=O and related to carbonyl groups in the hemicellulose structure [21,22].

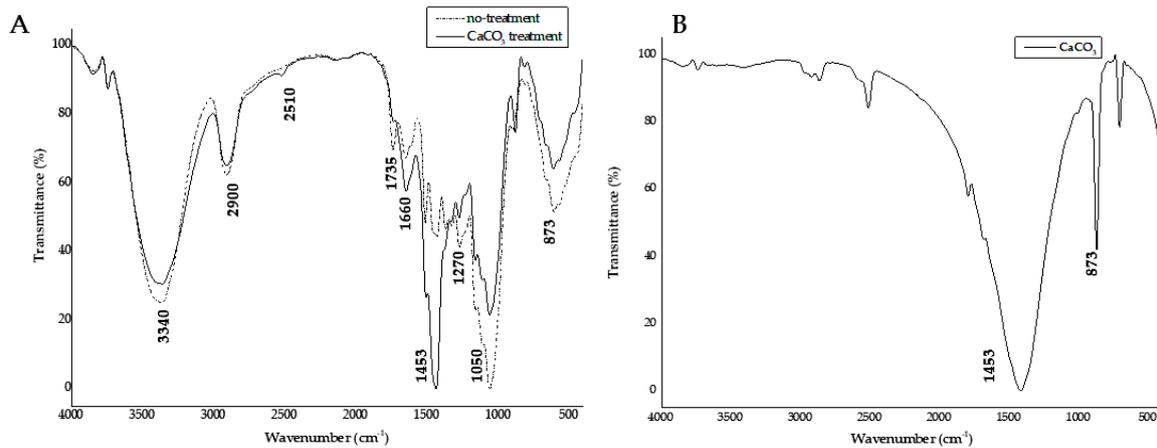


Figure 4. FTIR analysis, (A) untreated and treated wood samples and (B) CaCO_3 standard.

3.4. Thermogravimetric Analysis

TGA of the untreated wood samples showed a large signal at $367\text{ }^\circ\text{C}$, which implied a mass loss of almost 80% (Figure 5a). In contrast, the samples previously treated with CaCO_3 showed a different thermal degradation profile. It is possible to observe in Figure 5b the important increase of the signal (shoulder) near $300\text{ }^\circ\text{C}$ that appeared in the untreated samples. This signal in CaCO_3 -treated samples appears at lower temperatures ($283\text{ }^\circ\text{C}$) with a DTG of $-3.87\%/ \text{min}$. The DTG curve of CaCO_3 -treated samples presents two important decomposition stages: the first one appears as a signal in the form of a slight curve after $200\text{ }^\circ\text{C}$, and the second stage presents the highest peak of decomposition near $350\text{ }^\circ\text{C}$. In all replicates, the mineralized samples showed a maximum decomposition peak before that of untreated wood. Therefore, these TGA results suggest that, at the beginning, CaCO_3 -treated wood lost weight faster than untreated wood; however, after $350\text{ }^\circ\text{C}$, the opposite behavior was observed, and the untreated wood lost weight faster (Figure 5a), reaching a loss of about 92% compared with a weight loss of only 64% of the CaCO_3 -treated samples.

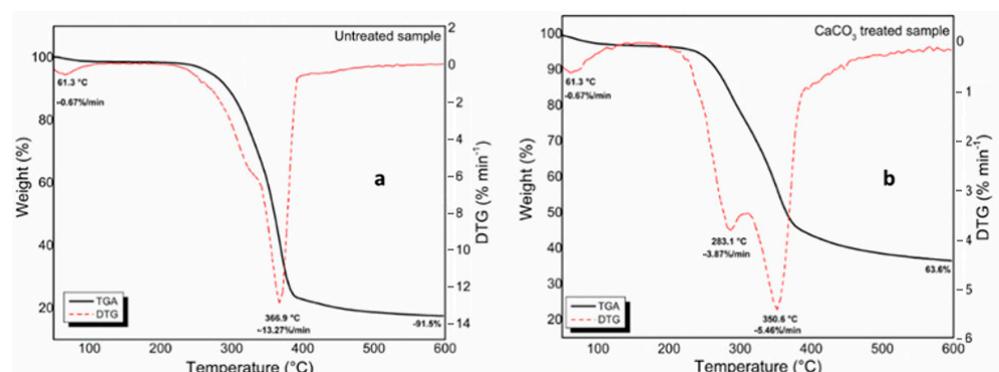


Figure 5. TGA and DTG analysis of (a) an untreated wood sample and (b) a sample treated with CaCO_3 .

3.5. Fire Resistance of the Wood Samples

The weight gain of the mineralized samples in the fire-resistance test is shown in Table 2. The results of the fire resistance tests are summarized in Figure 6. The ANOVA

results, available as Supplementary Data (Figures S2 and S3) show differences between the treatments (p -values < 0.05). Thus, a significant improvement in fire resistance was observed for the mineralized samples treated with four cycles of CaCl_2 30% compared to the control samples left without treatment. However, differences between the mineralized samples and those treated with the commercial fire-retardant agent AF7000 were not significant. In terms of weight losses, the mineralized samples reached an average value that was about 20 percentage points lower than that of the samples treated with the fire-retardant agent and more than 40 percentage points lower than that of control samples. A similar trend was observed for the carbonization index, which was almost 30 percentage points lower for the mineralized samples compared to the samples treated with the retardant agent and approximately 60 percentage points lower compared to the control samples.

Table 2. Weight gain of wood samples mineralized for the fire-resistance tests.

Sample	Weight Gain (%)
1	7.86
2	9.07
3	10.47
4	7.75
5	8.67

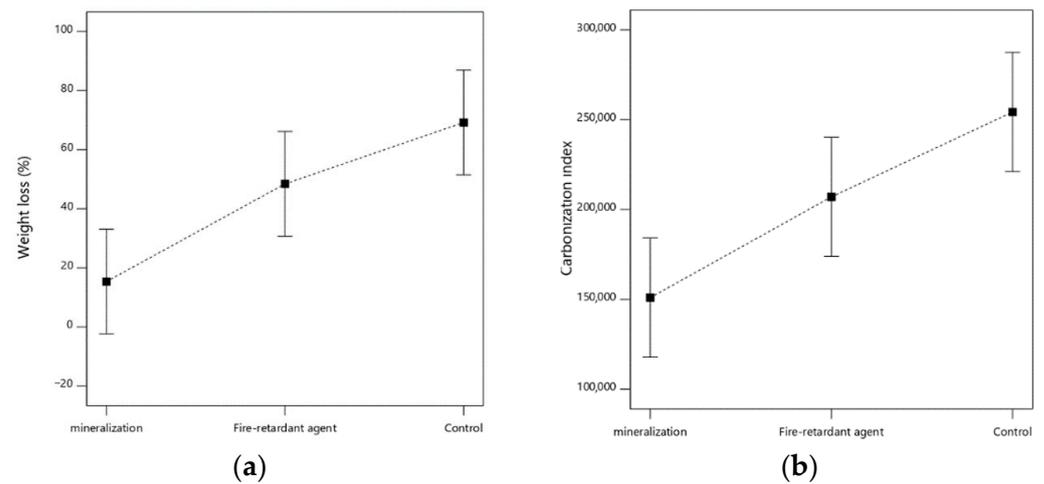


Figure 6. (a) Average weight loss and (b) carbonization index of mineralized wood samples, samples treated with the fire-retardant agent AF7000, and controls without treatment. Error bars depict the least significant difference (l.s.d.) after analysis of variance ($p < 0.05$).

The appearance of the wood samples after the fire-resistance test is shown in Figure 7. It can be observed that the mineralized samples maintained their structural integrity, which was not the case for some of the samples treated with the fire-resistant-agent and for the control samples. The integrity of the mineralized samples supports their reliability if used in a wooden structure subjected to fire, pointing out the great potential of the mineralization treatment for wood fire protection.

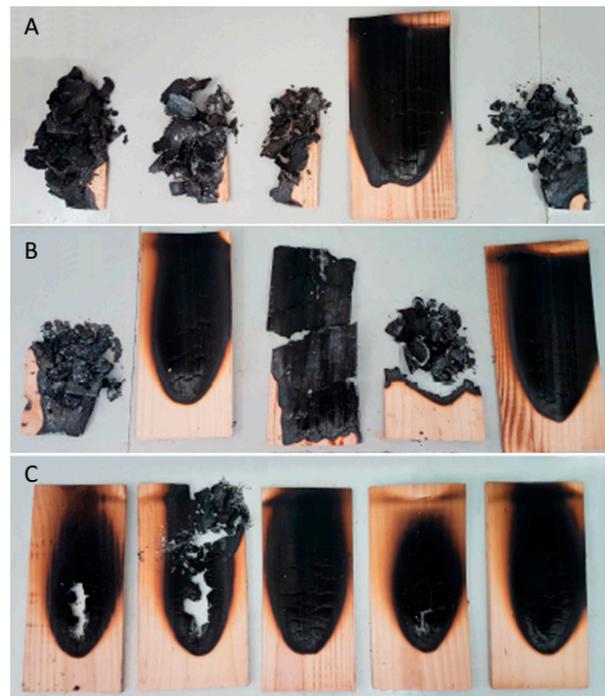


Figure 7. Wood samples after the fire-resistance test. (A) control samples; (B) samples treated with the fire-retardant agent AF7000; (C) CaCO₃ mineralized samples.

4. Discussion

The results obtained in this work support the hypothesis that a mineralization treatment based on wood impregnation with an aqueous solutions of CaCl₂, followed by sequential diffusion of ammonia and carbon dioxide, promotes CaCO₃ deposition into the wood microstructure, resulting in improved fire resistance and in the accumulation of CO₂. In the process of mineralization, the main product synthesized on the surface and inside the wood was CaCO₃. In the process, CO₂ reacted in presence of CaCl₂ in an alkaline environment (NH₃) to form CaCO₃. The best conditions of mineralization reached for radiata pine sapwood led to a weight gain of 20 wt.%, with an average of 0.467 (mmol·g⁻¹ wood) of CO₂ captured into the wood.

A significant increment of weight due to the mineralization after cycle 4 was apparently made difficult by the saturation of the wood surfaces and penetration pathways with CaCO₃. These pathways may include pits, rays, and cell lumens in a transverse section. In support of this, SEM images and EDS analysis showed a compact layer of minerals on the wood surface and a scarce presence of CaCO₃ at 10 mm depth. The ideal process of wood mineralization requires that the reaction occurs from the center of the sample towards the surface. In most mineralization processes, this is difficult to achieve, as the precursors of the chemical reaction are all first available at the surface, and consequently, the synthesis of minerals and byproducts will inevitably saturate the surface after several cycles of replications, if not during the first. In this case, diffusion of gaseous CO₂ apparently occurs in parallel with the formation of CaCO₃. In such conditions, it is likely that gaseous CO₂ would follow only free passages in the microstructure of the wood, avoiding the already coated surfaces and clogged lumens. Further testing, increasing CO₂ pressure or reaction times and using methods to promote the liberation of pathways before CO₂ injection into the system (such as sonication), may be valid strategies to improve the efficiency of the treatment.

Changes detected by FTIR, specifically, the decrease in absorbance of the band 1735 cm⁻¹, suggest a chemical interaction between CaCO₃ impregnated in the wood and the hemicellulose matrix. Evidence of this has been attributed to the absorption of calcium cations into pectin and lignin surfaces, which are rich in metal-complexing groups and are neg-

actively charged [14]. The TGA results showed that the mineralized samples degraded faster at the beginning of the test, but after 350 °C, this behavior reversed, and finally the untreated samples were more extensively degraded. These results are in agreement with those reported previously in the literature for different CaCO₃-treated samples [15,23]. It has been proposed that a fast initial degradation of CaCO₃-treated wood samples was due to the early degradation of CaCO₃, H₂O, and CO₂ [24] before reaching 100 °C (Figure 5). However, at higher temperatures (>350 °C), CaCO₃-treated samples become more stable to combustion due to aragonite transforming into calcite at 387 °C [25], which afterwards is decomposed into CaO and CO₂ at temperatures above 850 °C [26].

In terms of fire resistance, it is relevant to remark that the conditions of mineralization—CaCl₂ 30% and 4 cycles—only produced a weight gain of 8 wt.% for the fire-resistant test samples. This may be due to the presence of heartwood within large samples, which is more difficult to impregnate than sapwood. Despite this, the results showed that the mineralized samples performed to a similar level as the samples treated with a commercially available fire-retardant agent, while maintaining their structural conformation. This suggests the great potential of the treatment. The experimental results indicated that the main portion of the synthesized CaCO₃ was located at the surface of the samples, which is also the main area coming in contact with fire. Thus, it appears that, in terms of fire resistance, the specific concentration of CaCO₃ at the wood surface is more relevant than the total amount of CaCO₃ accumulated within the sample.

The mineralization of wood with CaCO₃ has been proposed by several authors to increase wood's fire resistance, but to our knowledge, a method comprising sequential gas diffusion has not been reported. Most of the reported treatments use liquid diffusion of CaCl₂ in combination with a number of agents, such as sodium hydroxide and supercritical carbon dioxide [23], aqueous sodium carbonate with dodecanoic acid [11], sodium bicarbonate [14,15,27], ammonium carbonate [28], sodium carbonate, alkaline hydrolysis of dimethyl carbonate [17], and calcium dimethylcarbonate in methanol [13]. In addition, a novel method was recently proposed consisting in impregnating wood with calcium acetoacetate [16]. The mineralization treatment used in this work yielded weight gains that were comparable to those obtained by using sodium bicarbonate and calcium acetoacetate as precursors [14,16], generating weight gains close to 35% for spruce samples and of about 28% and 8.3% for beech samples.

Common drawbacks of CaCO₃ mineralization treatments include the impossibility to achieve a deep deposition of minerals, the toxicity of certain precursors, and the complexity of the treatments. Although this was partially confirmed for the treatment proposed in this study, as certainly gaseous ammonia can be categorized as toxic, the diffusion of ammonia, in practical terms, can be achieved in a closed system in which the residual gases can be recovered and recycled. In addition, it is expected that the increment of reaction time with NH₃ and CO₂ may also increase the weight gain and the depth of mineralization.

The development of new and innovative technologies for fire protection capable of meeting the current environmental demands is a necessity. The method presented in this paper indicates that it is possible to promote the deposition of CaCO₃ inside the wood microstructure using a hybrid process that includes the use of liquid and gaseous reagents, resulting in the retention of CO₂ and improving wood's fire resistance. This opens the way for the development of wood products with enhanced performance and environmental characteristics that can be very attractive for many final users.

5. Conclusions

A mineralization treatment consisting in the impregnation of wood with CaCl₂ and subsequent sequential gaseous diffusion of NH₃ and CO₂ resulted in the accumulation of CO₂ in the form of CaCO₃ and in the enhancement of the fire-resistance properties of the treated wood samples. In the best conditions, the treatment yielded weight gains of about 20 wt.%, corresponding to an accumulation of 0.467 mmol·g⁻¹ (anhydrous wood) of CO₂ in the wood structure. In less favorable treatment conditions, the same methodology yielded

a weight gain of about 8 wt.%, which was sufficient to provide fire resistance similar to that of a commercially available fire-retardant agent. Further research, increasing CO₂ pressure and reaction times and using physical and mechanical methods to promote the liberation of circulation pathways inside wood before CO₂ injection, is advisable in order to improve the efficiency of the treatment. The application of in situ CaCO₃ deposition in wood can result in wood products with enhanced performance and environmental characteristics, supporting their sustainable development for wood construction and manufacture.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/coatings12010072/s1>, Figure S1: Analysis of variance of CaCO₃ mineralized samples; Figure S2: Analysis of variance of weight losses after the fire-resistance test; Figure S3: Analysis of variance of the carbonization index after the fire-resistance test.

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