Effect of dolostone fillers on the durable properties of mortars

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Research Article

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Abstract

This paper investigates the durable performance of well-curing mortars with varying replacement levels of dolostone filler (0–30% by mass) in comparison with the same replacement of limestone filler and the stability of mortars with dolostone filler for 2 years at 40 oC. Compressive strength, total porosity, capillary water absorption, and chloride migration coefficients were determined. Results show that compressive strength decreases, and the total porosity increases with increasing filler content due to a dilution effect, regardless of the filler composition. The capillary water absorption and the chloride migration coefficients rise significantly for mortars with 20–30% filler. But, the dolostone filler cements have lower chloride coefficients than those with limestone blended cements. Mortars with dolostone show no length changes without later reduction of compressive strength, and XRD and FT-IR analyses suggest the formation of hydrotalcite-like phases.

1. Introduction

The cement industry commonly incorporates limestone filler as a supplementary cement material (SCM) to reduce the clinker factor. Initially, using limestone filler allowed for increased cement production without significant investment. In the 1990s, European standards permitted its use as a minor component (< 5%) of cement [1], and later, ASTM C150 also endorsed this practice. Due to its economic viability, the environmental benefits (such as reduced carbon footprint), and the technical advantages (e.g., improved packing, formation of carbo-aluminates stabilizing ettringite [2–4] the limestone filler has become the most widely used SCM, accounting for approximately one-third of global SCMs [5].

Most cement standards allow limestone filler as a partial replacement ranging from 5 to 35% by cement mass. For instance, ASTM C595 incorporated cement Type IL containing 15% limestone filler by mass in 2012. European countries have used cements with up to 35% limestone filler since the late 1990s. Canadian standards (CSA A 3000 2007) permit incorporation between 5 and 15%, while Australian standards allow up to 12%. In 2015, India introduced a composite cement standard. The EN 197-5 2021 standard is the only one that accepts the use of dolostone filler in composite cements with a high content of slag additions.

In 2015, 195 countries signed the Paris Agreement, acknowledging their responsibility to reduce greenhouse gas emissions [6]. The production of Portland clinker is associated with significant CO₂ emissions, 800 kg CO₂/t cement (530 kg CO₂ being released for decarbonation of limestone [7] and the rest released by fuel combustion, transport within the plant and milling [5] Despite the environmental impact, the production of Portland clinker remains prevalent due to factors like raw material availability, technological maturity, and market adoption. Strategies for CO₂ reduction, as outlined in the GCCA roadmap [8], involve reducing the clinker factor in cement and decreasing cement content in mortar and concrete. These goals necessitate significant research into the composition and performance characteristics of traditional and new SCMs.
Several researchers [9–12] have explored the influence of dolostone filler on cement performance. Zajac et al. [13] and Xu et al. [14] investigated the hydration products and compressive strength of dolostone filler cement at different temperatures, revealing the formation of Mg-Al compounds, like hydrotalcite (Ht), contributing to the later strength.

Machner et al. [15–18] demonstrated that Ht-formation is influenced by pore solution alkalinity of the pore solution and the portlandite content in cement paste. In addition, Ht enhances durable properties, such as leaching and carbonation resistance, as well as chloride ion binding. However, studies on the effect of dolomite [9] on the durable properties of pastes, mortars, and concretes are limited. John et al. [19] appealed for detailed research on using lower-quality and high-Mg content limestone. Recent reviews [1, 6] emphasize the need for further investigation into SCMs other than limestone filler, particularly regarding their properties and durability.

This paper is part of a systematic investigation of the performance of dolostone fillers as SCMs. Previous studies [20–22] demonstrated that the physical-mechanical properties of cement pastes with 0, 10, 20 and 30% replacement by mass by dolostone or limestone filler with similar granulometry cured at 20 ± 2 °C depend on the percentage of filler incorporated rather than their mineralogical composition. The current study aims to explore the durable performance of mortars with varying replacement levels of dolostone or limestone filler after 28 days of water curing and to determine the volumetric stability of mortars with 20% by mass of dolostone filler over an extended period.

2. Materials

Mortars were formulated using normalized sand (EN 196-1), ordinary portland cement (OPC - CEM I according to EN 197-1), and dolostone and limestone powder obtained by grinding rock. Dolostone rock was obtained from the quarry of PolceCal S.A. at Sierras Bayas city, and the limestone was from the quarry at La Cabañita operated by Cementos Avellaneda S.A.; both quarries are located at SW in the Tandilia System, near Olavarría city (Buenos Aires Province, Argentina). Detailed geological, petrography, and mineralogical characteristics of the carbonate rocks and the production of both fillers have been previously reported [21]. Table 1 summarises the chemical composition determined by XRF, the physical properties, and the particle size distribution (PSD) parameters measured with laser diffraction (Malvern Mastersizer 2000E). The PSD of dolostone filler (DF) is bimodal (modes at ~ 3 and 20 µm), and limestone filler is trimodal (modes at ~ 3, 40 and 200 µm). These PSD curves are analogous up to 100 µm particle size, and limestone filler has a small volume (20%) of larger sizes. For OPC, the PSD curve is unimodal (mode at 30 µm), having coarser particle sizes than both fillers (d10 and d50 are 4 to 7 times smaller) [20].
Table 1
Chemical composition and physical properties of the materials.

<table>
<thead>
<tr>
<th>Chemical components (wt%)</th>
<th>Cement</th>
<th>Dolostone</th>
<th>Limestone</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>20.21</td>
<td>3.59</td>
<td>8.06</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>3.81</td>
<td>0.63</td>
<td>0.98</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>4.01</td>
<td>0.82</td>
<td>0.68</td>
</tr>
<tr>
<td>CaO</td>
<td>60.30</td>
<td>30.60</td>
<td>51.52</td>
</tr>
<tr>
<td>MgO</td>
<td>0.53</td>
<td>19.40</td>
<td>0.32</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>3.08</td>
<td>0.02</td>
<td>0.04</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>1.06</td>
<td>0.21</td>
<td>0.12</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.05</td>
<td>0.06</td>
<td>0.04</td>
</tr>
<tr>
<td>LOI</td>
<td>2.50</td>
<td>44.78</td>
<td>37.80</td>
</tr>
</tbody>
</table>

Physical characteristic

<table>
<thead>
<tr>
<th>Density (g/cm$^3$)</th>
<th>3.13</th>
<th>2.86</th>
<th>2.76</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific surface area Blaine (m$^2$/kg)</td>
<td>336</td>
<td>614</td>
<td>713</td>
</tr>
<tr>
<td>d$_{10}$ (µm)</td>
<td>2.97</td>
<td>0.52</td>
<td>0.62</td>
</tr>
<tr>
<td>d$_{50}$ (µm)</td>
<td>21.77</td>
<td>2.34</td>
<td>3.22</td>
</tr>
<tr>
<td>d$_{90}$ (µm)</td>
<td>58.42</td>
<td>23.79</td>
<td>174.81</td>
</tr>
</tbody>
</table>

The properties of cement pastes with 0, 10, 20 and 30% replacement by weight for dolostone or limestone filler (the effect on packing, fluidity, heat released and setting time) were analyzed in previous publications [20, 23].

3. Mortars

Dolostone filler (DF) and limestone filler (LF) were dry-mixed with ordinary portland cement (OPC) at different replacement levels, 0, 10, 20, and 30% by mass. For each blended cement, mortars were elaborated according to EN 196 using a sand-to-cement ratio of 3 and a water-to-cementing material (w/cm) ratio of 0.5 by mass.

Compared to the M-C0, the mortar flow increased or remained for 10% replacement, and it is slightly reduced (2–3%) for 20% replacement and further reduced (6–10%) for 30% replacement as previously described and justified [20].
The proportions, identifications, and properties of the studied mortars at 28 days are summarised in Table 2.

### Table 2
Proportion of blended cements (%) and properties of the mortars studied at 28 days of curing.

<table>
<thead>
<tr>
<th>Mortars</th>
<th>OPC</th>
<th>DF</th>
<th>LF</th>
<th>Compressive strength</th>
<th>Pore volume</th>
<th>Capillary absorption</th>
<th>Chloride migration</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-C0</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>M-C10DF</td>
<td>90</td>
<td>10</td>
<td>-</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>M-C20DF</td>
<td>80</td>
<td>20</td>
<td>-</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>M-C30DF</td>
<td>70</td>
<td>30</td>
<td>-</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>M-C10LF</td>
<td>90</td>
<td>-</td>
<td>10</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>M-C20LF</td>
<td>80</td>
<td>-</td>
<td>20</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>M-C30LF</td>
<td>70</td>
<td>-</td>
<td>30</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>

### 4. Methods

#### 4.1 Compressive strength and porosity

The mortars were cast in 40 mm x 40 mm x 160 mm moulds for compressive strength testing according to EN 196-1. After 24 hours in a moist cabinet (20 ± 2 ºC, RH > 90%), the samples were demolded and then immersed in water at 20 ºC for 28 days. The results are the average of three prisms. The relative compressive strength (CSI, %) is calculated as the ratio of the compressive strength of the mortar with DF or LF to the M-C0 mortar.

The total porosity was determined according to the ASTM C642 standard, with the average value of four cubic specimens (40 mm) reported.

Porosity was assessed on pastes with w/cm of 0.50, mixed and stored in plastic bags in a water bath at 20 ± 2°C until 28 days for different filler replacements, and they were named P-C0, P-C10DF, P-C20DF, P-C30DF, P-C10LF, P-C20LF and P-C30LF. The paste was ground in isopropyl alcohol to stop the hydration, and the non-evaporable water (Wn) was determined using the procedure proposed by Powers [24]. Finally, the hydration degree (α) was estimated assuming that filler is a chemically inactive addition and that the water needed for the complete hydration of the OPC is 0.195. The hydration degree was determined as
the ratio of $W_n$ and the water required for the total hydration of cement, according to Brouwers [25–26]. The gel–space ratio ($X$) and the capillary porosity ($\Phi = \frac{w}{c} - 0.37 \times \alpha \times 10$) were calculated using the Powers equations. Additionally, the pore fraction of the cement-filler systems was assessed by estimating the porosity of pure pastes ($\text{cfw} = \text{cement} + \text{filler} + \text{water}$) as $\text{cfw} = \left(\frac{W_n}{\text{effective} \ w/c}\right) \times 0.01$, neglecting the entrapped or entrained air and the effect of filler on the degree of hydration, as proposed by Damineli et al. [12].

### 4.2 Durable properties of mortars

The capillary water absorption test (ASTM C1585, called sorptivity tests) on six 40 mm cube mortars was determined at 28 days. Specimens were dried at $50 \pm 2^\circ\text{C}$ up to constant mass, and the lateral surfaces were sealed and exposed to water. In the sorptivity test, the mass changes are recorded at regular intervals during the 6 hours and later every day for the next 9 days. Water absorption by unit area was plotted as a function of the square root of time, and the initial sorptivity rate ($S_i$) was determined as the slope of the curve from 0.25 to 6 h using the least squares method when $R^2 > 0.98$. The secondary sorptivity rate ($S_s$) was determined using the slope of the same measurements between 1 and 7 days, but since the $R^2$ is less than 0.98, the determination is not reported, and only the capillary water absorption is reported as the weight increase per unit area of the cross-section of the specimen in g/mm$^2$ for the time in which the weight variation is less than 0.1% between two successive determinations.

Two cylindrical specimens of 100 mm diameter and 50 mm thickness were tested for each mortar as described by the NT BUILD 492 method. The non-steady-state migration diffusion coefficient ($D_{nssm}$) was calculated according to Eq. 1.

$$D_{nssm} = \frac{0.0239 \times (273+T) \times L}{(U-2) \times t} \times \left( x_d - 0.0238 \times \sqrt{\frac{(273+T) \times L \times x_d}{U-2}} \right)$$

Eq. 1

Where $D_{nssm}$ is the non-steady-state migration coefficient ($\times 10^{-12}$ m$^2$/s), $U$ denotes the value of the applied voltage (V), $T$ represents the average of the initial and final temperature of KOH solution of test setup ($^\circ\text{C}$), $L$ is the thickness of the specimen (cm), $x_d$ is the average value of chloride ions penetration depth (mm), and $t$ is the duration of the experiment (h) [27].

### 4.3 Volumetric stability of dolostone filler

Eight 25 mm×25 mm×250 mm moulds were filled with the M-C0 and M-C20DF mortars and placed in a humid chamber at $20 \pm 2^\circ\text{C}$ for 24 h. After demolded, the initial length of four mortar bars with end studs was recorded. Bars were immersed in water in a hermetic recipient and stored at $40 \pm 2^\circ\text{C}$. At 28, 90, 180, 360 and 720 days, the length change of bars and the compressive strength on six 25 mm cubes were determined.

At 720 days, several mortar slices were cut, immersed in isopropanol for 7 days, and dried in a vacuum dissecator at $20 \pm 2^\circ\text{C}$ for 48 h. A mortar slice was crushed to pass through a 45 µm sieve and analyzed
by X-ray diffraction (XRD) and FT-IR. Other mortar slices were covered with Au/Pl and examined with a Carl Zeiss scanning electron microscope, EVO MA10.

5. Results and discussion

5.1 Compressive strength and porosity

Figure 1 shows the compressive strength at 28 days as a function of the percentage of filler incorporated. Replacing 10 to 30% of DF or LF in cement reduces the compressive strength due to the dilution effect. However, the reduction consistently remains below the replacement percentage. These findings align with previous studies [28] in mortars with the identical replacement of dolostone or limestone filler cured at 40 °C for 28 days and those reported by other authors cured at 20 ºC [29–30] [15]. It is concluded that strength reduction depends on the percentage of filler incorporated rather than its mineralogical composition (dolostone and limestone).

Figure 1 also shows that the total porosity at 28 days increases with the filler percentage (DF or LF) increase, agreeing with previous research [31]. Compared with the M-C0 porosity (dotted line), the porosity increased by ~ 3, 13, and 25% for mortars with 10, 20 and 30% filler, respectively. This increase is comparable to the findings of Moon et al. [32] (13.5 and 26.5% for 25 and 35% LF, respectively) and Machner et al. [15], emphasizing that incorporating filler of both carbonate sources (DF or LF) in more than 5% by mass leads to increased porosity.

The Powers model has been employed to elucidate the performance of limestone filler cement [3, 33–35]. According to this model, compressive strength and porosity result from the gel/space ratio in the paste that depends on the water-cement ratio, the degree of hydration, and the volume of entrapped air. The filler content affects this structure due to the dilution effect, measured as an increase of w/c proportionally to filler content [36–38]. The nucleation effect is caused by finer filler particles that stimulate the early hydration of cement [39–43] and the chemical reaction of filler that changes the assembly of the paste (for calcareous filler AFm phases) [44–49].

Table 3 reports the Wn, the effective w/c ratio, the degree of hydration ( ), the gel-space ratio (X), the capillary porosity (φ) and the cwf of the pastes after 28 days of curing.
Table 3
Wn, effective w/c, α, X and Φ of the pastes cured at 28 days.

<table>
<thead>
<tr>
<th>Paste</th>
<th>Wn</th>
<th>effective w/c</th>
<th>α</th>
<th>X</th>
<th>φ</th>
<th>cwf</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-C0</td>
<td>15.83</td>
<td>0.50</td>
<td>0.81</td>
<td>0.740</td>
<td>0.20</td>
<td>0.32</td>
</tr>
<tr>
<td>P-C10DF</td>
<td>17.19</td>
<td>0.56</td>
<td>0.88</td>
<td>0.729</td>
<td>0.23</td>
<td>0.31</td>
</tr>
<tr>
<td>P-C20DF</td>
<td>18.21</td>
<td>0.63</td>
<td>0.93</td>
<td>0.700</td>
<td>0.28</td>
<td>0.29</td>
</tr>
<tr>
<td>P-C30DF</td>
<td>18.86</td>
<td>0.71</td>
<td>0.97</td>
<td>0.654</td>
<td>0.36</td>
<td>0.27</td>
</tr>
<tr>
<td>P-C10LF</td>
<td>17.60</td>
<td>0.56</td>
<td>0.90</td>
<td>0.740</td>
<td>0.22</td>
<td>0.31</td>
</tr>
<tr>
<td>P-C20LF</td>
<td>17.51</td>
<td>0.63</td>
<td>0.90</td>
<td>0.682</td>
<td>0.29</td>
<td>0.28</td>
</tr>
<tr>
<td>P-C30LF</td>
<td>20.90</td>
<td>0.71</td>
<td>~1</td>
<td>0.702</td>
<td>0.32</td>
<td>0.29</td>
</tr>
</tbody>
</table>

The Power’s model considers dolostone and limestone as fillers or diluents. Dilution reduces the volume fraction of cement in the system while holding the volume fraction of water constant. Consequently, the effective water-to-cement ratio of the system is increased, leading to enhanced hydration and reduced chemical shrinkage. Adding filler increases the effective w/c ratio from 0.50 in P-C0 to 0.56, 0.63 and 0.71 in pastes containing 10, 20 and 30% of filler. Then, the maximum percentage of fillers is also limited by the w/cm ratio used in the mixtures that increment the space to be filled by the hydration products. If the effective w/c ratio increases over 0.42, capillary pores should be presented in the fully hydrated system.

Finally, the compressive strength is related to the gel-space ratio, which measures all effects produced by adding fillers (acceleration of hydration, dilution and increase of effective w/c ratio). Figure 2 shows the compressive strength and the total porosity as a function of the gel-space ratio (X) obtained from a curve fitting of experimental data corroborating this relationship for both fillers and indicating that the optimum level of fillers is a function of the mixture proportions [47].

A previous paper shows that MIP evaluates the pore size distribution as first intrusion [20]. The total pore volume is quite similar for all pastes, the threshold pore width is similar, and the critical pore diameter is ~65 nm. Phung et al. [50] determined that the total porosity of pastes with 10 and 20% filler does not change significantly when the w/cm ratio decreases proportionally to the filler content and the porosity is similar to the OPC paste.

### 5.2 Durable properties of mortars

Capillary water absorption is a transport mechanism widely used to characterize the resistance to water absorption by capillarity, and it is related to pore structure and connectivity [51]. Figure 3 shows the capillary water absorption as the square root of the time for mortars after 28 days of curing. These curves present two parts; the first linear part (S₁) is related to the filling of coarse capillary pores, whereas the second part is associated with the filling of smaller pores by inhibiting the secondary rate (S₂) [51]. The total amount of absorbed water, also called capacity, is related to the total porosity, pore size, and connectivity of the pores [52]. Figure 3 also includes the capacity and the initial rate of water absorption.
(Si) as a function of the filler content. M-C10DF and M-C10LF show the same capacity as M-C0 as reported in other experimental research [53–54].

In contrast, the total water absorptions of mortars with 20 and 30% replacement by DF or LF were higher. However, the Si of mortar specimens with fillers was close to the reference specimen. That may be because although adding filler increases the tortuosity of the pore system, it is impossible to compensate for the dilution effect. The capillary water absorption capacity increases for equivalent replacement percentage in mortars with DF compared to mortars with LF.

With a few exceptions, the increased filler substitution level generally increased the capillary water absorption of the mortars compared to the reference specimen, whereas the effect on the Si was more limited. Luc and Frédéric [55] report that sorption is directly related to the pore diameter. Initially, when mortar comes into contact with water, the large pores suck more water, and the finer filler particles reduce the pore section causing a low Si coefficient.

These results are consistent with the total porosity of the corresponding mortar specimens. As the added filler content increases, the total porosity of the mortar increases, and the capacity increases. The open porosity is growing between 0% and 15% substitution of cement by limestone filler, as described by Luc and Frédéric [55]. The results indicate that concretes containing up to 10% limestone generally have lower depths of water penetration than concretes, and concretes containing more than 10% limestone show greater depths [56]. In cementitious materials, water transport depends on the capillary porosity (volume, connectivity, and tortuosity) related to the w/c ratio and the hydration degree. For OPC pastes with a w/cm = 0.50, Irassar [57] reported that capillary porosity becomes disconnected when the hydration degree is approximately 0.93. When increasing the filler, a lower w/cm is required to reduce the capillary porosity due to the dilution effect. For example, the disconnection of capillary pores was obtained using a w/cm of 0.50, 0.48, 0.43 and 0.34 for blended cement containing 5, 10, 20 and 35% filler, respectively.

The chloride coefficient (\(D_{\text{nssm}}\)) of mortars obtained by migration is shown in Fig. 4. The \(D_{\text{nssm}}\) of the mortars with filler exceeded that of the standard mortar (upper the dotted line) and increased with the percentage of filler incorporated. It also included the \(D_{\text{nssm}}\) increase expressed as a percentage of standard mortar, showing a significant difference between DF and LF, increasing with the replacement percentage. The dilution effect is predominant over the hydration acceleration, and then chloride penetration increases with high limestone content [58].

Corrosion of steel bars has become the most critical problem affecting the durability of reinforced concrete structures and chloride ingress has been identified as the main cause of steel corrosion in concrete. Diffusion is the primary mechanism of chloride ion transport in concrete, and the chloride diffusion coefficient is used to characterize the performance of concrete [59].

Firstly, the resistance to chloride migration of the mortar increases as the porosity decreases since water mobility, and therefore of chloride ions, is reduced [60]. For LF, a good correlation is found between the \(D_{\text{nssm}}\) and the total porosity of the mortars at 28 days (12.856*\(e^{0.0099x}\), \(R^2 = 0.97\)) and the \(D_{\text{nssm}}\) had an
exponential increment for 30% of replacement, when the total porosity overpass the 18% guaranteed high connectivity of the pore structure [59] instead the complete hydration of clinker in the blended cement. Li et al. [59] demonstrated that a high LF replacement is detrimental to concrete's porous structure, leading to a higher chloride diffusion coefficient.

Luc and Frédéric [61] tested cement replacement with limestone filler (0, 15, 23 and 27% by mass) with a w/mc ratio of 0.45, agreeing that chloride penetration increases with the percentage of filler incorporated. However, the porosity of mortars with LF and DF is similar [20], and mortars with LF show a higher $D_{nssm}$. It has been shown that the correlation between porosity and chloride ingress is very good when the same cement is studied, but it does not hold when changing the chemical composition of the cement since it affects the ability to bind chlorides [62].

On the other hand, Machner et al. [18] reported that pastes with (40% w/w replacement) dolomite or dolomite-metakaolin cured at 38 or 60°C contributed significantly to the chloride binding. However, at 28 days, hydration has not fully developed, and chloride migration tests describe a situation of reduced chloride binding [60], so the reduction in chloride ingress cannot be fully attributed to the chemical binding.

Noushini et al. showed that, although there is no chemical binding of chlorides, it is possible to reduce chloride ingress. Therefore, it is assumed that the ions can be adsorpted or bind without forming Friedel's salt [63]. At the same time, the physical binding of chlorides in the hydrated phases of the cement paste can retard the ingress of chlorides [64], which reduces the $D_{nssm}$.

Therefore, given the test conditions and the porosity of the mortars under study, the reduction of $D_{nssm}$ in the mortars with DF with respect to those with LF is attributed to the increase in chloride adsorption in the hydrated phases of the mortars with DF.

### 5.3 Volumetric stability of dolostone filler

Figure 5 shows the evolution of the compressive strength and the length variation of the M-C0 and M-C20DF mortars submerged in water for 720 days at 40 ± 2 °C. The compressive strength of M-C0 (Fig. 5a) slightly increased up to 90 days and remained practically constant up to 720 days. For M-C20DF, compressive strength remains constant until 360 days and then grows to 720 days.

The change in length of the M-C0 mortar (Fig. 5b) shows a slight expansion (0.03%) at 90 days, and the length remains constant. The expansion/contraction of M-C20DF bars does not present a defined trend that could indicate an expansion process caused by the dedolomitization reaction as time passes at this temperature; they indicate the volumetric stability of mortars with DF. The dotted lines (Fig. 5b) represent the length variation (± 0.03%) attributed to the thermal variation of the mortar bar during the measure. The thermal coefficient of mortar varies between 7.9 and 12.6 $\times$ $10^{-6}$ m/°C [65], then the bar length varies between 0.039 and 0.063 mm for a measurement made at 20 or 40 °C, which represents a length change between 0.01 and 0.03%.
After 720 days submerged in water at 40 ± 2 ºC, the visual appearance of the mortar specimens (Fig. 6), M-C0 and M-C20DF are free of cracks in corners and alterations on the surface.

The XRD patterns of M-C0 and M-C20DF are illustrated in Fig. 6. For M-C0, ettringite (Et) and portlandite (P), OPC hydration products, are assembled with unhydrated C$_4$AF, calcite (C) from OPC and carbonation, and quartz (Q) from the sand. For M-C20DF, C$_4$AF, Et and P from OPC are complemented with calcite and dolomite (D) from DF and Q mainly form sand, and a new phase like hydrotalcite type (Ht, $\theta = 11.5^\circ$) is identified. Preliminary results at one year [20] identified a change in the main peak intensity ratio between dolomite and calcite, revealing dedolomitization or carbonation during the measurement.

The FT-IR spectra of the M-C0 and M-C20DF are shown in Fig. 7. In the OH$^-$ stretching bands (Fig. 7a), a clear peak can be observed at 3643 cm$^{-1}$ assigned to the OH in portlandite and the typical band corresponding to the stretching vibrations of water (v(O-H)) at 3430 cm$^{-1}$. The absence of a very sharp peak at 3690 cm$^{-1}$ indicates the lack of brucite (B), a typical product of dedolomitization [66–67]. At 1644 cm$^{-1}$ (Fig. 7b), the deformation of the water bond v(H-O-H) is detected. The characteristic strong bands of carbonates remain (at 1431 cm$^{-1}$, corresponding to v$_3$ of the CO$_3^{2-}$ group and at 728 cm$^{-1}$, corresponding to v$_4$), and the bands between 970 and 1100 cm$^{-1}$ are associated with C-S-H. Disproportion on the dolomite/calcite compound is revealed in the FT-IR spectra of C20DF paste at 28, 365, and 720 days, where the band at about 712 cm$^{-1}$ assigned to calcite increases and the absorption of the band at 728 cm$^{-1}$ assigned to dolomite decreases as suggested by Lipus [68]. The detail in Fig. 7 shows that the peak at 875 and 712 cm$^{-1}$ characteristic of the carbonates, as expected, was more evident in the mortars with DF. Ht presents a broadened peak at 3530 cm$^{-1}$, which could not be assigned because it is within the water deformation band. However, the incipient band at 651 cm$^{-1}$ assigned to Ht is observed in the M-C20DF, coinciding with what was demonstrated by XRD, without evidence for a harmful dedolomitization in accordance with previous investigations [26,55; 58].

For DF, a more stable Mg-Al double layer hydroxide (LDH) phases, similar to Ht, generally exhibit poor structural order and are thought to occur as a solid solution of the form Mg$_{(1-x)}$Al$_x$(OH)$_{(2+x)}$(H$_2$O) where 0.20 $\leq x \leq$ 0.33 when there is CO$_2$ deficiency in the system [48]. Several authors [9, 28, 69] agree that the later growth in compressive strength could be associated with the formation of Ht, which would explain the increase in compressive strength of the M-C20DF mortar after 360 days of curing (Fig. 5a).

Figure 8 shows the SEM microphotographs at 500X and 1000X of the mortars M-C0 and M-C20DF after submerged in water for 720 days at 40 ºC. In mortar M-C0 (Figs. 8a and 8b), the crystals of ettringite in the form of needles are developed in the pores, forming structures that resemble a grid [70]. For M-C20DF, the portlandite crystals in thin hexagonal platelets appear in pores, corroborating the results of XRD and FT-IR.

6. Conclusions
Figure 9 serves as a comprehensive visual representation of the relative performance indices of mortars incorporating dolostone filler (DF) and limestone filler (LF) in comparison to the standard mortar (M-C0). The x-axis depicts the relative index for DF, while the y-axis illustrates the relative index for LF.

After 28 days, the compressive strength of the mortars is predominantly influenced by the filler percentage, irrespective of the filler's mineralogy. The total porosity of mortars at 28 days increases proportionally with the filler content, with LF-containing mortars exhibiting a more pronounced rise.

The Si and capillary water absorption capacity of the mortars containing 10% filler cured at 28 days are comparable between DF and LF and slightly lower than the standard mortar. However, for 20 and 30% filler replacements, the Si and capillary water absorption capacity increases, with DF-containing mortars showing a more significant rise.

All the mortars with filler at 28 days exhibit higher chloride migration coefficients than the standard mortar. This coefficient rises as the filler percentage increases, with LF-containing mortars demonstrating a more unfavourable trend.

In summary, the performance of mortars with dolostone filler aligns closely with those incorporating limestone filler. Mortars with 0% and 20% DF, as partial replacements for OPC with a w/mc of 0.50, exhibit enduring compressive strength and minimal length variations after 720 days submerged in water at 40 ± 2 °C. Mineralogical analyses through XRD and FT-IR reveal that dolomitization promotes the formation of a phase like hydrotalcite in dolostone-containing mortars without the formation of deleterious brucite, affirming the sustained non-detrimental impact of dolostone filler in the cementitious matrix over time. These findings underscore the potential of dolostone filler as a sustainable and resilient alternative in concrete applications.

References


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**Figures**
Figure 1

Compressive strength and total porosity as a function of the % of filler.
Figure 2

Compressive strength and total porosity at 28 days as a function of the gel/space ratio of Power's model.
Figure 3

Capillary water absorption of mortars cured at 28 days and capacity and Si as a function of the % of filler.  

a) M-C0 and M-DF; b) M-C0 and M-LF.
Figure 4

Chloride migration coefficient of mortars cured at 28 days.
Figure 5

M-C0 and M-C20DF submerged in water at 40 ± 2 °C for up to 720 days,
a) Variation in compressive strength; b) Variation in the length of the mortar bar.
Figure 6

Visual appearance and XRD pattern of the filtered solids of M-C0 and M-C20DF after remaining submerged in water at 40 ± 2 °C for 720 days. (Et = ettringite, Ht = hydrotalcite; P = portlandite; Q = quartz, C = calcite and D = dolomite)
Figure 7

FT-IR spectra of the solids filtered from the M-C0 and M-C20DF mortars immersed in water at 40 ± 2 °C for 720 days.
Figure 8

SEM microphotographs with SE1 detector of mortars immersed in water for 720 days at 40 °C, a) M-C0 at 500 X, b) M-C20DF at 500 X, c) M-C0 at 1000 X, d) M-C20DF at 1000 X.
Figure 9

Comparison of the performance of mortars with DF and LF.