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ORIGINAL ARTICLE

Mechanical evaluation and hydration kinetics of cement pastes with dolomitic filler

Avaliação mecânica e cinética de hidratação de pastas de cimento com fíler dolomítico

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Abstract: The scarcity of high-purity limestone subjects the cement industry to consider alternative supplementary cementitious materials for cement production. This research aimed to investigate the mechanical properties and the hydration kinetics of cement pastes in the presence of high levels and different fineness of dolomite, especially the formation of thaumasite. A dolomite filler with 20% magnesium oxide, with average diameters of 10 µm, 6 µm and 4 µm was used as a partial replacement for Portland cement at 0%, 15% and 35% in cement pastes cured at 5 ºC and 20 ºC. The results of compressive strength showed similarities in all pastes analyzed, but the fineness of the dolomite showed a significant difference between the strengths obtained. The isothermal calorimetry indicated that the presence of dolomite had a nucleation and dilution effect. The thermogravimetry revealed that dependent of the substitution levels, the pastes with dolomite presented significant differences in the amount of ettringite and carbonate phases. The mineralogical analysis detected the presence of thaumasite only at the temperature of 20 ºC, which this mineral can also form at higher temperatures than those reported in the literature. Finally, we conclude positively about the possibility of using dolomite in cementitious matrices at levels up to 35%, regardless of fineness and curing temperature.

Keywords: dolomitic limestone, filler, hydration, thaumasite.

Resumo: A escassez de calcário de alta pureza sujeita a indústria cimenteira a considerar materiais cimentícios suplementares alternativos para a produção de cimentos. Esta pesquisa buscou investigar a cinética de hidratação e as propriedades de pastas cimentícias na presença de elevados teores e diferentes finuras de dolomita, em especial à formação de taumasita. Adotou-se um fíler dolomítico com 20% de óxido de magnésio, de diâmetros médios de 10 µm, 6 µm e 4 µm como substituto parcial do cimento Portland nos teores 0%, 15% e 35% em pastas cimentícias curadas a 5 ºC e 20 ºC. Os resultados de resistência à compressão apresentaram semelhanças em todas as pastas analisadas, mas a finura da dolomita mostrou uma diferença significativa entre as médias de resistências obtidas. A calorimetria isotérmica apontou que a presença de dolomita apresentou efeito de nucleação e diluição. A termogravimetria revelou que dependente dos teores de substituição, as pastas com dolomita apresentaram diferenças significativas na quantidade de fases de etringita e carbonatos. A análise mineralógica detectou a presença de taumasita apenas na temperatura de 20 ºC, em que esse mineral também pode se formar em temperaturas mais elevadas do que as temperaturas relatadas na literatura. Por fim, conclui-se positivamente sobre a possibilidade de utilização de dolomita em matrizes cimentícias em teores de até 35%, independente da finura e da temperatura de cura.

Palavras-chave: calcário dolomítico, fíler, hidratação, taumasita.

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1 INTRODUCTION

The cement industry generates negative environmental impacts, such as carbon dioxide (CO_2) emissions during cement production and degraded areas for mining raw materials. The sector is responsible for about 8% to 9% of global CO_2 emissions released annually into the atmosphere [1]. With increased awareness of these large-scale emissions, interest in mitigation strategies has increased, including a variety of approaches such as consideration of equipment efficiency, fuel substitution (including increased use of biofuels), use of alternative feedstocks, and use of supplemental cementitious materials [2]. Thus, cement with high filler contents has been explored.

In addition, the dosage by particle packing is a technique that has been used to increase the content of carbonaceous material and decrease cement consumption in the production of concretes [3]. Hunger [4] mentions that packing is linked to selecting the proper proportion and size of particles so that larger voids are filled with smaller particles. Thus, the author explains that particle packing has some advantages for concrete properties, both in the fresh and hardened state. When fine particles are added to the mix, they help to fill the voids in the structure, leaving minimal space for water. Thus, the fine particles cause a decrease in concrete porosity and also minimize the consumption of cement paste.

In the search for references, one notices that most of the studies using calcareous filler refer to calcite. On the other hand, doubt arises about using dolomitic limestone filler, especially dolomite, with high magnesium oxide (MgO) content. Dolomitic limestone is a magnesium calcium carbonate mineral, $CaMg(CO_3)_2$, abundant in nature in the form of dolomitic rocks, with MgO content typically ranging between 4 and 10%. The dolomite, in turn, has MgO content ranging between 19% and 22% [5]. Unlike calcareous limestone, dolomite is not as accepted as supplementary material in cementitious matrices because some forms of dolomitic aggregates can cause deleterious effects on concrete due to dedolomitization and related expansive reactions.

However, it has already been reported that adding dolomite in powder form is not problematic and, when added to cement, has a compressive strength similar to that of Portland cement [6], [7]. Szybilski and Nocuń-Wczelik [8] proved in their study this accelerating effect, they further highlighted that at the low percentage of incorporation, dolomite plays a cement replacement role, and at a higher dosage, the dilution effect is observed. However, the authors comment that the increase in dolomite content is accompanied by higher amounts of hydrated products due to the crystallization of the fine dolomite grains and better water absorption. Machner et al. [9] investigated the potential use of dolomite limestone instead of calcite as an addition to Portland cement with metakaolin (5, 10 and 20% dolomite addition), observing the development of compressive strength at curing temperatures 5º, 20º and 38 ºC. The authors point out that the addition of dolomite affects Portland cement with metakaolin, similarly to the addition of calcareous limestone. Both result in the formation of additional monocarboaluminate (AFm) phases and ettringite stabilization and can be used to replace part of the Portland cement with metakaolin without impairing the compressive strength. The study further adds that at low addition levels, they can even improve strength. In the case of dolomite, the positive effect was not visible at 5 °C, but the strength was increased when cured at 38 °C. The authors mention that dolomite can replace 10% cement without compromising strength at 20 °C or 38 °C. The study also points out that the reactivity of dolomite can be increased by raising the curing temperature.

Magnesium released from dolomite can also interact with the aluminates in the cement to form hydrotalcite, which causes a decrease in porosity and an increase in compressive strength [10]. However, there is still no consensus in the literature about the interaction of dolomitic limestone in the cement hydration process under different replacement contents and curing temperatures, making it necessary to investigate the parameters of the reactions.

Zajac et al. [10] and Lou [11] point out that the presence of limestone and magnesium oxide (MgO) can favour the formation of thaumasite, which, according to Rahman and Bassuoni [12], occurs in the presence of calcium ions, silicate, sulfate, carbonate and water. The authors further mention that low temperatures favour its formation. Zhou et al. [13] explain that the presence of magnesium oxide in contact with water hydrates forming magnesium hydroxide ($Mg(OH)_2$), also known as brucite, and during the hydration reaction, the formation of an expansive gel can be observed. The study further mentions that this expansion stresses the structure, which can cause cracking and lead to future concrete disintegration. Szybilski and Nocuń-Wczelik [8] investigated the performance of dolomitic limestone in cement hydration. They observed that increasing the dolomitic limestone content is accompanied by a more significant amount of hydration products as a result of the crystallization of the fine grains of dolomite. However, the researchers do not clarify the actual result of the chemical interaction of dolomitic filler with cement. Zajac et al. [10] mention that there is no technical justification for excluding dolomites from a cement composition because the chemical reaction between dolomite and clinker results mainly in hydrotalcite ($Mg_6Al_2CO_3(OH)_{16}$-$4(H_2O)$), with no expansion diagnostic. Justnes [14] considers the properties of dolomitic limestone to be better than those of calcitic limestone because it acts as a filler in the mixture and does not cause expansion. On the other hand, other studies point out that the presence of dolomite can cause expansion due to the formation of thaumasite.

The formation of thaumasite occurs when there is the simultaneous presence of sulfates, carbonates (existing in limestone or dolomite aggregate), water and low temperatures (around 15 ºC) [15], [16]. Sulfate-resistant Portland cement does not prevent thaumasite formation because they have lower aluminate contents that react with sulfates to form ettringite [17].

However, John et al. [18] point out that using limestone filler with high MgO content in the cementitious matrix can be considered an innovative technology. The authors also point out, however, that the study of durability as the parameters of carbonation, shrinkage and sulfate attack is still not well understood so far. In this context, this research aims to investigate the hydration of Portland cement in the presence of dolomite filler under different substitution levels and fineness of this mineral.

2 MATERIALS AND EXPERIMENTAL PROGRAM

The materials used were Portland cement CP V-ARI for having a lower content of additions in its composition and dolomitic limestone filler with an average grain size of 18 µm. This cement is equivalent to CEM I EN 197 [19] and ASTM C150 type III [20], due to the low content of pozzolanic additions. Two base formulations were produced with the replacement of cement by dolomite at 15% wt and 35%, by mass, and a reference formulation without modifications. These materials chemical and physical compositions are shown in Table 1 and the mineralogical characterization is illustrated in Figure 1.

Table 1. Chemical and physical composition of cement and dolomitic limestone filler.

	Properties		CP-V ARI	Dolomitic Limestone Filler
Chemical Composition (% w.t)	Silicon Dioxide (SiO_2)		16.56	12.26
	Aluminium Oxide (Al_2O_3)		2.56	0.92
	Iron Oxide (Fe_2O_3)		4.23	0.74
	Calcium Oxide (CaO)		60.60	28.72
	Magnesium Oxide (MgO)		1.87	20.11
	Sulfuric Anhydride (SO_3)		2.11	ND
	Sodium Oxide (Na_2O)		1.21	0.09
	Potassium Oxide (K_2O)		2.10	0.14
	Titanium Oxide (TiO_2)		0.51	0.04
	Phosphorus Pentoxide (P_2O_5)		0.09	0.02
	Chromium Oxide (Cr_2O_3)		0.01	ND
	Manganese Oxide (MnO)		0.15	0.03
	Zinc Oxide (ZnO)		0.04	ND
	Strontium Oxide (SrO)		0.36	0.01
	Loss on Ignition (LOI)		7.61	37.43
Physical Characteristics	BET Specific Area (cm^2/g)		16.40	18.60
	Specific Mass (g/cm^3)		2.94	2.81
	Granulometric Analysis	D_{10} (µm)	3.64	4.12
		D_{50} (µm)	10.26	17.86
		D_{90} (µm)	24.66	66.70
		Dm (µm)	11.82	24.88

ND = Not detected

The dolomite was not used in its original form and had its particle size adjusted by grinding to be finer than the binder to enhance the degree of hydration and provide heterogeneous nucleation effects. Alumina balls with a diameter of 2 cm were used as the grinding body. Thus, to achieve the D_{50} diameter of 10 µm, 4 hours of grinding in the horizontal ball mill was required, to achieve the diameter of 6 µm, 12 hours of grinding in the horizontal ball mill was required, and finally, to obtain 4 µm, 12 hours of grinding in the horizontal ball mill plus 1 hour in the eccentric horizontal mill was required. The physical results of the ground dolomitic limestone are shown in Table 2.

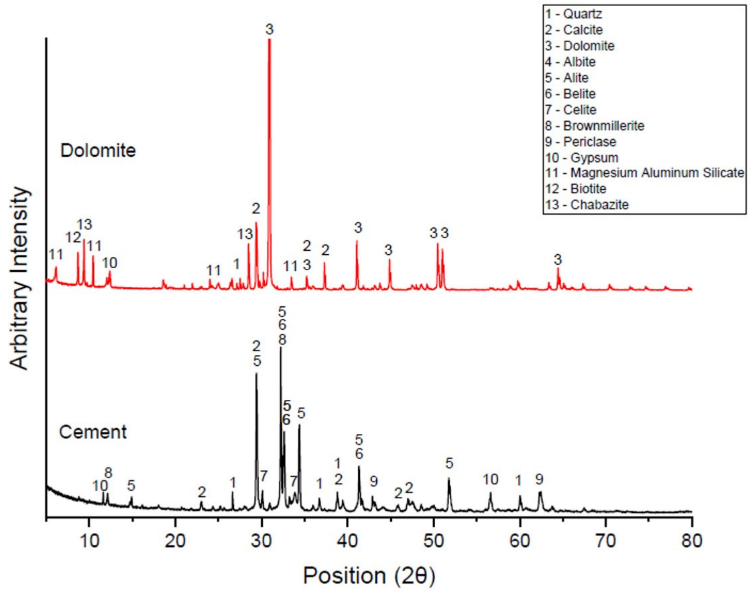

Figure 1. Mineralogical characterization of cement and dolomitic limestone filler.

Table 2. Physical characterization of dolomite after grinding.

Physical Characteristics		**Dolomite**		
		10 µm	**6 µm**	**4 µm**
BET Specific Area (cm^2/g)		35.500	31.000	71.200
Specific Mass (g/cm^3)		2.79	2.78	2.77
Granulometric Analysis	D_{10} (µm)	3.37	1.68	1.17
	D_{50} (µm)	10.69	6.64	3.99
	D_{90} (µm)	26.39	19.8	12.02
	Dm (µm)	12.27	8.28	5.10

The admixture used was a TEC FLOW 8000 type superplasticizer. The maximum amount of admixture to be added was determined based on the cement mass and the solid content so that there would be no change in the pastes water/cement (w/c) ratio.

The mixing of the pastes was performed in a mixer at 10000 rpm under controlled conditions of temperature 21°C ± 2°C and relative humidity of 60% ± 10%. According to the following procedure: homogenization of the dry materials in a plastic beaker using a glass rod, adding the water and the additive to the dry materials under manual mixing for 50 seconds and mechanical mixing for 90 seconds.

A w/c ratio of 0.48 was set for all pastes, with the consistency adjusted with superplasticizer additive as a function of the reference paste, with a spreading limit of 70 ± 3 mm. The method used to determine the consistency was the mini-slump test, developed by Kantro [21].

Table 3 shows the mixing ratios and dosage parameters for the pastes. The samples were identified as REF5 (reference paste cured at 5 ºC), REF20 (reference paste cured at 20 ºC), D15F10 (15% dolomite replacement with 10 µm fineness), D15F6 (15% dolomite replacement with 6 µm fineness), D15F4 (15% substitution by dolomite with fineness 4 µm), D35F10 (35% substitution by dolomite with fineness 10 µm), D35F6 (35% substitution by dolomite with fineness 6 µm) and D35F4 (35% substitution by dolomite with fineness 4 µm).

Table 3. Proportions and dosage parameters for formulations.

Formulations	**Curing temperature (ºC)**	**Quantity of material (g)**				**Slump Test (mm)**
		Cement	**Dolomite**	**Water**	**Chemical admixture**	
REF5	5	300	0	144	0	69
		300	0	144	0	
		300	0	144	0	
REF20	20	300	0	144	0	
		300	0	144	0	
		300	0	144	0	
D15F10	5	255	45	122.2	0.270	71
	20	255	45	122.2	0.270	
D15F6	5	255	45	122.2	0.270	70
	20	255	45	122.2	0.270	
D15F4	5	255	45	122.2	0.270	72
	20	255	45	122.2	0.270	
D35F10	5	195	105	93.6	0.598	72
	20	195	105	93.6	0.598	
D35F6	5	195	105	93.6	0.643	72
	20	195	105	93.6	0.643	
D35F4	5	195	105	93.6	0.682	69
	20	195	105	93.6	0.682	

After the production process, the pastes were molded in cylindrically shaped silicone molds with a diameter of 16.5 mm and a height of 33 mm. They were also compacted to remove air bubbles in a sieve shaker for one minute at the lowest speed. The samples were subjected to two temperature conditions 5 ºC (in a cold chamber) and 20 ºC (in a humid chamber), with a relative humidity of 100%.

The isothermal calorimetry was performed in a calorimeter model TAMAir, TA Instruments, to monitor the hydration kinetics of the pastes for 72 hours. It should be noted that this test was performed only at a temperature of 20 ºC. The results were normalized by total binder amount (cement + filler).

The thermal analyses (TG/DTG) were used to analyze the cement hydration development by quantifying the hydrated compounds formed and to obtain the portlandite mass loss (from 400 to 500 ºC), as well as the chemically combined water content (from 40 to 500 ºC). For this and considering that M is the molar mass, Wx is the percentage of mass loss under a temperature xºC, Equations 1 and 2 were used.

$$CH = \left(\frac{W_{60} - W_{500}}{W_{500}}\right)\frac{M(Ca(OH)_2)}{M(H_2O)} \tag{1}$$

$$BW = \frac{W_{60} - W_{500}}{W_{500}} \tag{2}$$

Finally, the X-ray diffraction (XRD) test was employed to analyze the characterization of the dolomitic filler and to identify the crystalline compounds, such as the presence of ettringite and thaumasite in the samples. The test was performed in a PANalytical diffractometer, Empyrean model, with an operating voltage of 40 kV and current of 40 mA, with an angular interval ranging from 5 to 60°, with a step of 0.1 and time of 50s in each step. The mineralogical analyses were analyzed using X'Pert HighScore Plus software, version 3.0.

The interruption of paste hydration for thermal and mineralogical analyses was performed at 28 days of age by solvent exchange according to the procedure described by Deschner et al. [22] and Schöler et al. [23].

The mechanical strength was evaluated from the compressive strength test, adapting the NBR 7215 standard [24], and the pastes ruptured at 7 and 28 days of curing. The test was performed in EMIC - INSTRON press, model DL-200, class I, with a load capacity of 2000 kgf, with an error less than 0.5% and a loading speed range of 0.008 mm/s.

3 RESULTS AND DISCUSSIONS

3.1 Isothermal Calorimetry

Figure 2 presents the heat evolution rate curves of the studied pastes, which show that the dolomite content changed the hydration speed of the mixtures and changes in the induction, acceleration, and deceleration periods of the reactions.

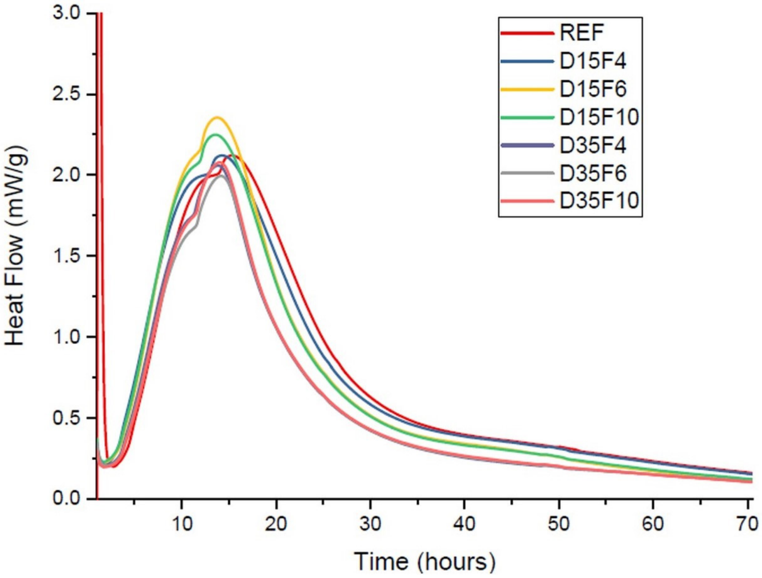

Figure 2. Rate of heat evolution.

The presence of 15% dolomite caused a higher heat flux rate in the acceleration stage, which according to the studies of Szybilski and Nocuń-Wczelik [8] and Elgalhud et al. [25], can be attributed to the nucleation effect of the limestone filler. This occurs because of the finer particles of the mineral addition that promote more available spaces for hydrate formation and act as sites for hydrate precipitation and growth [26].

Zhu et al. [27] point out that to effectively reduce the heat of hydration, a larger amount of limestone fines (more than 30%) is required in the concrete mix. At the 35% content, sulfate depletion occurs more rapidly when compared to the 15% dolomite content.

Investigating the influence of the studied fines, it is possible to visualize that at the 15% content, the 6 µm and 4µm fines presented the highest heat flow rates, followed by the 10 µm fines, which is consistent with the nucleation phenomenon. This same trend is not observed at the 35% dolomite content, with the behavior dominated by the dilution process. In this case, the 10 µm and 4µm fines showed similar heat flow rates, accompanied by the 6 µm fineness, with lower rates. A trend in the behavior of the mixtures based on the fineness parameter cannot be observed. The literature reports that increasing the fineness of limestone particles results in a more significant number of nucleation sites, promoting an acceleration in the hydration reaction of C_3S, an essential component of Portland cement, while other cement hydration reactions remain limited [28]. However, Briendl et al. [29] research mentions that divergent results can be observed regarding particle fineness and due heat fluxes, but they emphasize that there is no firm explanation for this behavior.

3.2 Thermal Analysis

Figure 3 illustrates the thermal analyses of all the mixtures produced, with the appropriate distinctions of the cementitious matrices.

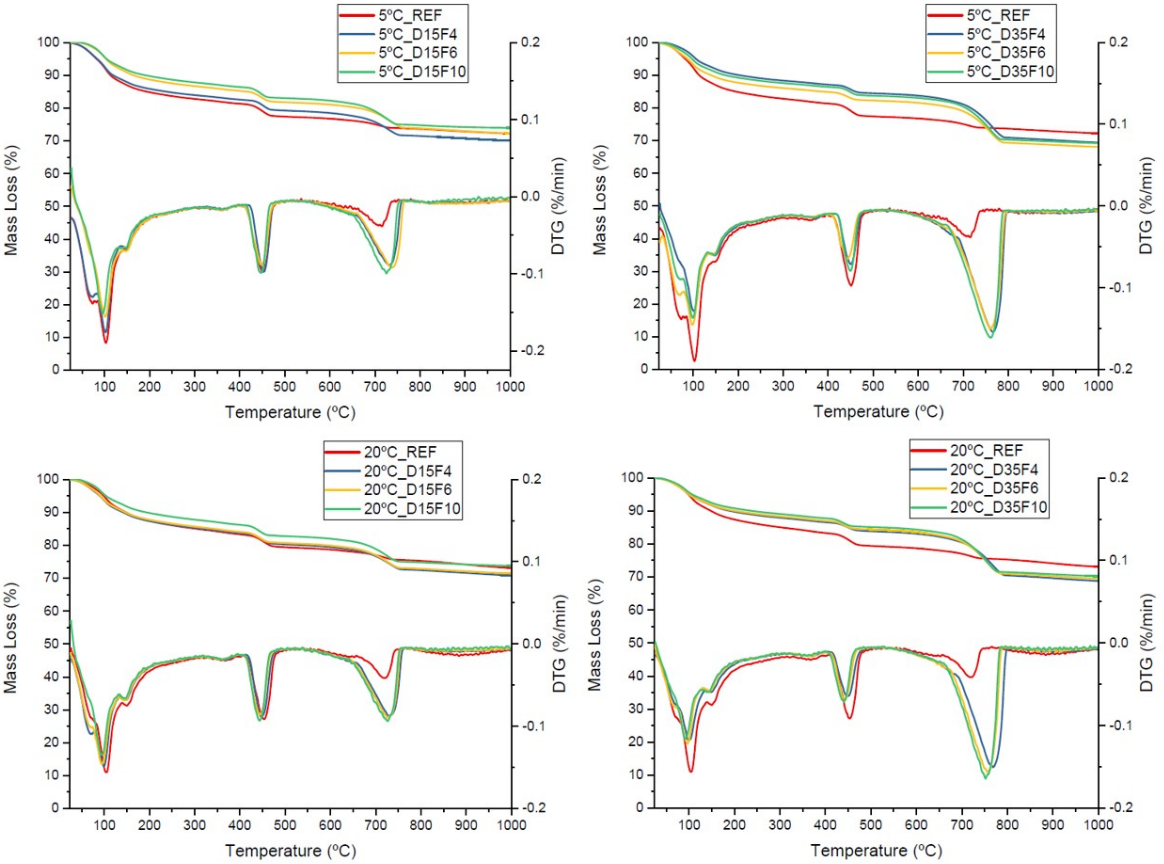

Figure 3. Thermogravimetry curves of the pastes.

It is observed, in all formulations, an endothermic peak around 100 ºC related to the decomposition of ettringite and the beginning of C-S-H dehydration, a small shoulder at 150 ºC referring to hemi/monocarbonate, a second peak around 450 ºC due to portlandite decomposition, with distinct areas for the events, and a third peak due to the decomposition of carbonates (calcium and magnesium) from 550 to 1000 ºC [30].

At dependent replacement levels, the samples with dolomite show notable differences in the amounts of phases produced since all samples with dolomite show lower decompositions, with the exception of the carbonate peak, compared to the REF sample with increasing curing temperature, a fact also observed by Machner et al. [9]. According to some authors, filler is not inert and reacts chemically with Portland cement. The hemi/monocarbonate phases are formed from the reaction of limestone with the C_3A of the binder and are more stable than monosulfate in the presence of carbonates. This chemical effect results in an increased volume of hydrated compounds and provides higher compressive strength to cementitious materials with low levels of offset [31]–[33].

The derived thermogravimetry made it possible to calculate the portlandite ($Ca(OH)_2$) content and the chemically combined water at 28 days of hydration of the pastes, as presented in Table 4.

Table 4. Portlandite and combined water content at 28 days of the pastes.

Formulations	Portlandite at 5 ºC	Portlandite at 20 ºC	Combined water at 5 ºC	Combined water at 20 ºC
REF	16.13	14.53	28.43	25.62
D15F4	13.02	12.67	25.46	24.03
D15F6	12.56	12.49	22.28	23.41
D15F10	13.08	12.84	20.44	20.81
D35F4	9.19	9.40	18.20	18.84
D35F6	8.44	8.93	20.72	18.14
D35F10	9.69	9.23	19.06	17.25

It can be seen that the REF sample, without incorporation of dolomite, was the one that decomposed more portlandite and the one that combined more water chemically due to holding a greater amount of reactive phases, both at 5 ºC and 20 ºC, which can be compared with the results of calorimetry for 72 hours where it was more reactive and due to the hydration reactions of the CP-V ARI occurring at early ages.

It is also observed that all mixtures, at both temperatures, did not present a more significant decomposition of portlandite about the REF sample due to the absence of pozzolans and the increased content of fillers in their compositions. With the increase of dolomite, there is a reduction in the decomposition of $Ca(OH)_2$, except for samples D15F10 and D35F10. This is possibly due to the presence of the dolomite filler that may have intensified the hydration reactions, providing more nucleation points for the increase in the amount of hydrated products.

From another perspective, samples D15F10 and D35F10 decreased the portlandite decomposition at 28 days by 19% and 40% at 5 ºC, respectively, compared to the reference paste. For the temperature of 20 ºC, there was a decrease of portlandite at 28 days by 12% and 36% for the same samples, respectively, compared to the reference paste. This means that the higher the content of dolomite incorporation with increasing curing temperature, the less the consumption of $Ca(OH)_2$.

The mixtures D15F4, D15F6 and D15F10 showed higher amounts of combined water, in that order, perhaps because the lower the fineness of the dolomite, the greater it is surface area, the greater demand for water to surround the grains for both temperatures of analysis and of similar trend presented by the mixtures with 35% dolomite incorporation at 20 ºC as follows: D35F4, D35F6 and D35F10. The values of the mixtures with 35% dolomite at 5 ºC seem very close without presenting the same behavior trend observed in the other variables.

Comparing the samples among themselves regarding the levels of incorporation and fineness of the dolomite, the amount of chemically combined water decreased with the increase of dolomite and the increase of fineness up to the 6μm samples in comparison with the reference samples. The dilution effect can explain this due to replacing reactive material with a less reactive material that resulted in the mentioned decrease in combined water, corroborating with the studies of Machner et al. [9].

The effect of different curing temperatures is similar for the portlandite and chemically combined water contents. The samples cured at 5 °C show the highest contents, and with increasing curing temperature, the results decrease. The decrease in combined water contents with increasing curing temperature can be attributed to the densification of the C-S-H phase at higher temperatures, being related to a decrease in its structural water [34], [35].

3.3 Mineralogical Analysis

The mineralogical analyses aided in detecting the products formed from the hydration of the cement with the dolomite limestone. Figure 4 presents the diffractograms of the samples cured at 5 ºC and the diffractograms of the samples cured at 20 ºC.

The diffractograms show the formation of different hydration products between the mixtures, showing that at 5 ºC, only the formation of ettringite was identified, and at 20 ºC, the presence of ettringite and thaumasite was detected. Data may reinforce Lou's theory [11], when mentioning that the crystal structure of ettringite is very similar to that of thaumasite; therefore, the two are confused in the literature.

At the curing temperature of 5 °C with the 15% dolomite content in all mixtures, it is possible to verify the formation of three crystalline peaks of higher intensities, portlandite, dolomite and ettringite. Peaks of lower intensities are identified in the mixtures. However, the compounds identified are different as the dolomite fineness increases. By increasing the dolomite content while maintaining the analysis temperature, the presence of other minerals is found, which was already expected because as the amount of cement in the paste was decreased, compounds characteristic of limestone rock appeared. The pastes produced with 35% dolomite present four crystalline peaks of higher intensities: dolomite, portlandite, ettringite, and biotite, peaks common in all mixtures. The same behavior trend observed in the pastes with 15% about the fineness, is present in the 35% content.

Analyzing the temperature of 20 ºC, in the 15% dolomite content, the same minerals formed at the temperature of 5 ºC are detected, but in all mixtures, the formation of thaumasite is identified. The same is observed in the 35% dolomite content, but the presence of gypsum was not observed in the mixtures. The reference pastes showed the formation of the same minerals at temperatures of 5 ºC, as at a temperature of 20 ºC, being observed the presence of portlandite, ettringite and calcite with peaks of higher intensities. Because of this, it is possible to note that all the minerals identified in the pastes, except for thaumasite, are part of the compositions of the materials used to produce them. Along these lines, the hypothesis to explain the development of this mineral in the samples cured at 20 ºC may be related to the presence of chabazite identified in the diffractograms or divergence is occurring in the literature regarding the identification of thaumasite and ettringite in the XRD test.

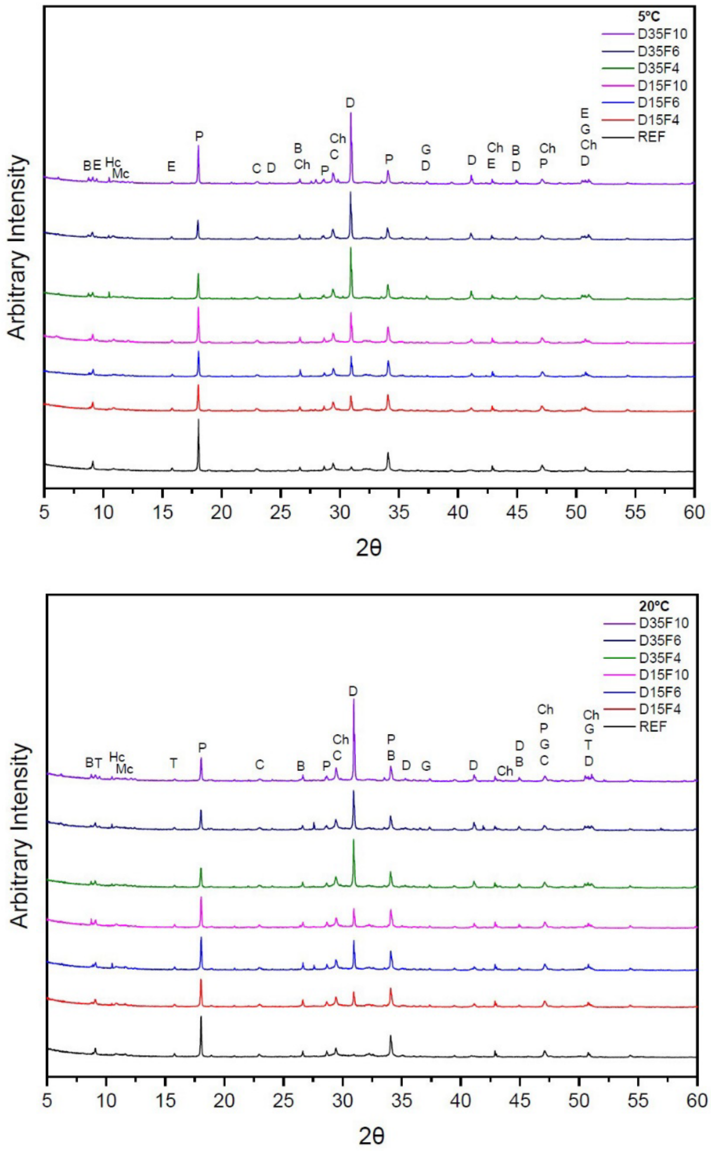

Figure 4. XRD of pastes cured at different temperatures. Legend: B = Biotite (ICSD 95359); Hemicarbonate (ICSD 163124); Monocarbonate (ICSD 59327); C = Calcite (ICSD 257807); Ch = Chabazite (ICSD 23913); D = Dolomite (ICSD 23913); E = Ettringite (ICSD 759497); G = Gypsum (ICSD 230283); P = Portlandite (ICSD 202220); T = Thaumasite (ICSD 31247).

It is important to note that the thaumasite identified in this paper does not refer to sulfate attack thaumasite (SAT). Słomka-Słupik and Zybura [36] propose a new term for this formation, called TnSA (thaumasite non sulfate attack), which means thaumasite without sulfate attack.

Also, by analyzing the results obtained, the formation of brucite and hydrotalcite was not detected in the mixtures, reinforcing the study of Barsi et al. [37]. The discussions about the non-use of dolomite in cementitious matrices are due to the fact that it contains magnesium in its composition, which can trigger the formation of expansive gels within the matrix. With the present study, it can be verified that the reaction of dolomite in cementitious systems is not necessarily considered to form harmful hydration products because the only compound identified as a result of the dolomite reaction with Portland cement was the portlandite.

3.4 Compressive Strength

The totality of the axial compressive strength results and the mean value and standard deviation for each formulation are presented in Figure 5. For the calculation, the values considered were those whose relative deviation was less than or equal to 5%.

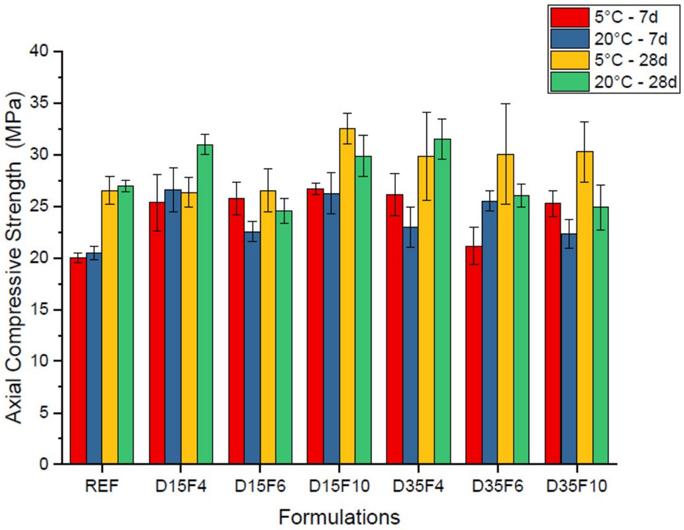

Figure 5. Average axial compressive strengths.

It is observed that all mixtures containing dolomite showed strength values equal to or greater than the reference when compared to the entire data set. When comparing the curing temperatures, it is possible to observe that at 5 ºC, at 7 and 28 days, formulation D15F10 presented the highest strength value. At 20 ºC, formulation D15F4 presented the highest resistance value at 7 days, and formulation D35F4 presented the best mechanical performance at 28 days. However, when the data set is analyzed, it can be observed that the temperature of 5 ºC presented the highest strength value, reaching approximately 33 MPa.

Mehta and Monteiro [38] emphasize that it is important to understand the possible effects of temperature on concrete properties at early ages. According to the authors, when samples are molded and kept at low temperatures at early ages, there is no improvement in the hydration process, which may contribute to strength loss. However, Cecconello and Tutikan [39] studied the influence of low temperatures on concrete strength evolution and observed that concretes cured at lower temperatures at early ages could contribute to strength increase. The authors explain that the longer the hydration of Portland cement takes, the better the crystalline structure formation will be, thus clarifying that concretes cured at low temperatures at early ages can have a superior mechanical behavior than those cured at higher temperatures. Under these conditions, hydration reactions may occur slowly, delaying the setting and hardening of concrete or not occurring due to lack of water. Machner et al. [9] identified an increase in compressive strength in the presence of dolomite at temperatures of 20 ºC and 38 ºC. In this study, it was also possible to identify an increase at a temperature of 5 ºC.

When analyzing the substitution content used, formulation D15F4 and D15F10 showed the highest strength values at 7 and 28 days, respectively. The mixture D35F4 demonstrates higher strength values at both 7 days and 28 days. The 15% and 35% contents presented similar compressive strength results. Thus, it can be stated that fineness 4 presents the best mechanical performance of the data set, which was already expected, because the smaller the particle size, the better the packing of the grains and, consequently, the higher the compressive strength. Palm et al. [40] corroborate this theory by reporting that part of the limestone particles should be ground more refined than the clinker to serve as nucleation sites and enhance the hydration process, raising the mechanical performance. However, Mikhailova et al. [7] point out that partial replacement of cement with dolomite results in an increase in compressive strength with a limit of up to 25% replacement, above which the authors describe a reduction in strength occurs. According to the authors, this is because the ultrafine particles (4 µm and 2.79 µm) of dolomite act as nucleation sites, where an increase in the rate of crystallization of silicates occurs, which facilitates the hydration of the Portland cement minerals.

The results of ANOVA and the F test indicated that for a 95% confidence interval, the variables age, temperature, and content showed no significant difference between the means of compressive strength. Only the fineness variable showed a significant difference in the compressive strength means, as shown in Tables 5 and 6.

Table 5. ANOVA.

Source of variance	*SQ*	*GL*	*MQ*	*F*	*P-Value*	*Critical F*
Between groups	35342.2	4	8835.6	124.6	4.9596E-80	2.38
Within groups	48922.0	690	70.9			
Total	84264.2	694				

Table 6. F Test.

	Axial compressive strength	*Fineness*
Average	27.08	5.71
Variance	19.72	10.84
Observations	168	168
GL	167	167
F	1.82	
P(F<=f) uni-caudal	6.366E-05	
F critical uni-caudal	1.29	

4 CONCLUSIONS

As for the axial compressive strength, it was evident that all mixtures containing dolomite showed strength values equal to or greater than the reference sample due to the fineness of the particles of the filler.

When investigating the hydration process of the cement pastes and in comparison with the reference paste, the 15% dolomite content caused a higher rate of heat flow, and when 35% dolomite was incorporated, there was a reduction in the heat flow rate. This indicates that dolomite's presence reduces the cement pastes accumulated heat.

The thermogravimetry curves revealed that independent of the substitution levels, the pastes with dolomite showed significant differences in the amounts of ettringite and carbonate phases since all pastes with dolomite indicated less decomposition compared to the reference paste with increasing curing temperature. It was also possible to analyze the portlandite and combined water content of the samples, which showed that the samples without the incorporation of dolomite were the ones that consumed the most portlandite and the ones with the most combined water chemically, both at 5 ºC and 20 ºC. With the increase of dolomite, it was verified that there is a reduction in the consumption of $Ca(OH)_2$.

The analysis of the mineralogical composition of the hydrated cement pastes by XRD allowed the identification of a behavioral trend of all mixtures, presenting a composition of the minerals found in both cement and dolomite, highlighting that at the temperature of 5 ºC only the formation of ettringite was identified and at the temperature of 20 ºC, the presence of ettringite and thaumasite was detected.

It was observed that the temperature of 5 ºC presented the highest strength value, reaching approximately 33 MPa. As for the dolomite content, the strength results were similar, indicating that both 15% and 35% dolomite presented superior mechanical performance compared to the other mixtures studied. As for the fineness, the D15F4 and D35F4 formulations expressed the highest strength values at 7 days and 28 days, indicating that the 4µm fineness presented the best performance.

Finally, it was possible to verify that incorporating fine particles and high magnesium content in the dolomite limestone, under these study conditions, indicates a potential use in cement pastes.

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