ANALYSIS OF THE INFLUENCE OF CARBONATE ADDITIONS ON THE STRENGTH OF MAGNESIUM OXIDE COMPOSITE

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ABSTRACT

This article deals with the study of a composite based on Magnesium Oxide (MgO) as a way to obtain a material that represents lower CO_2 emissions in its production compared to Portland cement or gypsum. The MOS composite was used, and various proportions of carbonate material (limestone powder) were incorporated to improve its properties and reduce the final product cost, enabling its application in civil construction. Samples containing only MgO and $MgSO_4$ (without limestone powder), referred to as 'Reference' (REF), were melted. Subsequently, 15%, 25%, 35%, and 45% of carbonate material were incorporated by mass, resulting in samples labeled as 'CALC15', 'CALC25', 'CALC35', and 'CALC45', respectively. After the wet curing process, the prismatic samples were tested for flexural strength and compressive strength. The expandability test was conducted using the Le Chatelier Apparatus. The results indicated that the incorporation of limestone powder proved to be beneficial in terms of strength gain for both flexural and compressive tests. To optimize both flexural and compressive strength, the best outcome was observed in the sample with 35% limestone powder incorporation (CALC35).

KEYWORDS: *Magnesium Cement, Magnesium Oxide Composite, MOS, Powdered Limestone.*

I. INTRODUCTION

This article focuses on the study of a composite based on Magnesium Oxide (MgO) as a means to obtain a material that produces lower CO_2 emissions in its production compared to Portland cement or gypsum.

Magnesium cement technology consists of mixing MgO and specific salts diluted in water and, when the salt used is Magnesium Chloride Hexahydrate, the composite obtained is known as "MOC". On the other hand, when the composite is formed by the salt of Magnesium Sulfate Heptahydrate, the composite obtained is called "MOS". This article deals with the study of MOS because there are few international scientific publications on the subject. However, the material has good characteristics to be used in the production of fence panels, as it has low weight, low alkalinity and good fire protection.

Additives and mineral mixtures can improve the properties of magnesium composites, as occurs in the properties of Portland cement, such as fly ash, silica fume and rice variety silica to modify the properties of MOC and MOS cements. [1] investigated the influence of the addition of pulverized fuel ash and ground granulated blast furnace slag as pozzolans. [2] studied the influence of the use of steel slag on the compressive and water strengths of MOS cement. [3]

analyzed the use of fly ash with low and high calcium contents, in the water resistance of MOS cements. The addition of fly ash to the MOC was studied by [4]. Rice Husk Silica (RHS) was added to MOS and MOC by [5]. [6], [7], [8] studied various types and proportions of carbonate materials in Magnesium Oxide (MgO) composites.

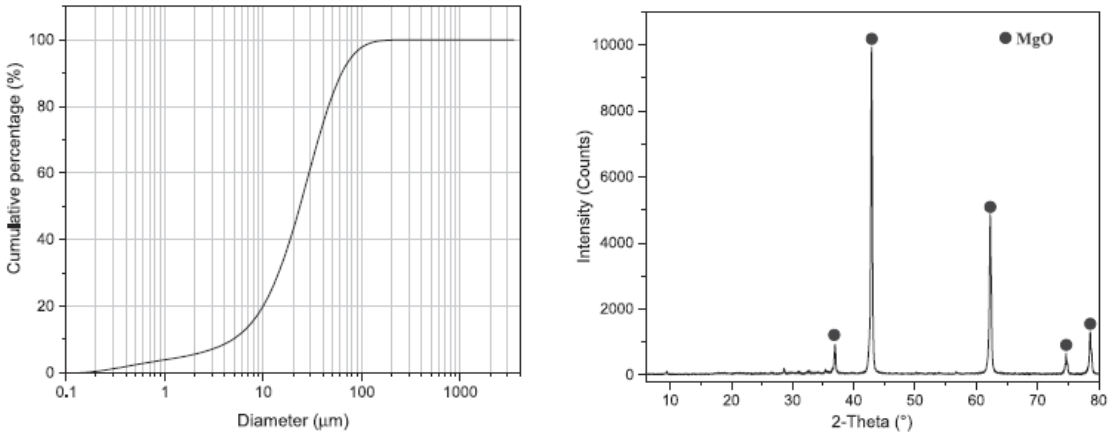
This research was carried out using the MOS composite and the incorporation of various proportions of the carbonate material (limestone powder) in order to improve its properties. With the use of this material, it is expected that the small size of the powdered limestone grains must have a beneficial effect on the composite, nucleating the formation reaction, in its densification and in the reduction of the final cost of the product, making possible the application of this material in civil construction. The choice of limestone as filler was because it is a very abundant and easily accessible sedimentary rock, in addition to being widely used in the composition of fiber cement composites.

The remainder of the text is organized as follows: Section II presents the employed methodology; results and discussion are presented in Section III and the main conclusions drawn from the study are presented in Section IV.

II. METHODOLOGY

2.1. Characterization of Magnesium Oxide

MgO used was manufactured and provided by IBAR Nordeste industry that extracts, benefits and calcines magnesite. The granulometric distribution and x-ray diffraction of Magnesium Oxide are shown in Figure 1 and Tables 1 and 2.



(a) (b)

Figure 1. a) grain size distribution curve b) X-ray diffraction

Table 1. MgO Chemistry Composition.

Mass Percentage (%)					
MgO	SiO_2	Al_2O_3	Fe_2O_3	CaO	MnO
91.74	3.99	0.21	2.14	1.75	0.17

Table 2. MgO physical properties.

Specific Area (m^2/g)	Diam. (µm)		Specific Mass (g/cm^3)
	D(50)	D(90)	
7.25	23.5	62.5	3.58

2.2. Characterization of Limestone Powder

Ray Diffraction (DRX) was used, by equipment XRD-6000 Shimadzu, made in the Chemistry Institute Lab of Federal University of Uberlandia and its results are showed in Figure 2.

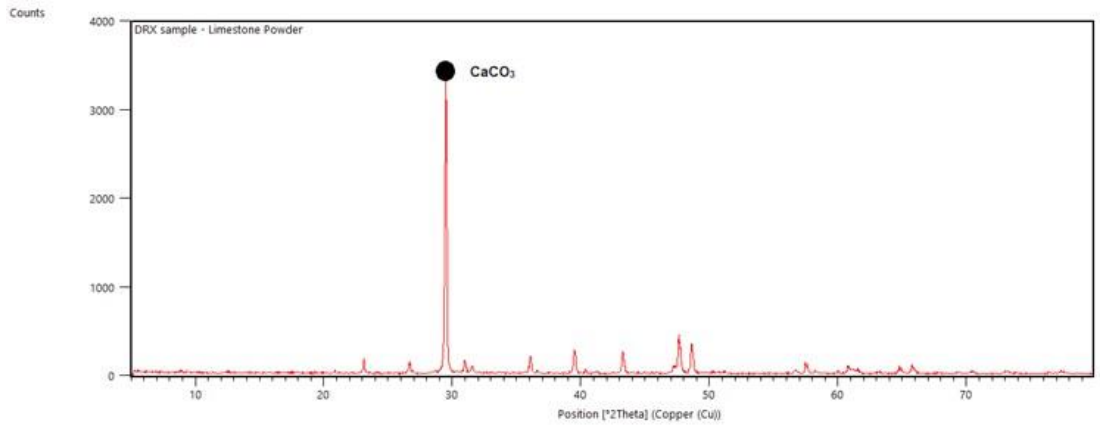


Figure 2. X Ray Diffraction of the limestone powder

The unit mass of the limestone powder was determined in accordance with [9]. To determine the specific mass, a standard related to Portland cement [10] was used, due to the similar granulometry of both limestone and cement. The granulometry of the limestone powder was determined by [11]. The limestone powder was placed in a mechanical spreader, and the procedures were followed as prescribed by [12]. After homogenizing the mixture, the sedimentation test began. Readings were taken with a densimeter and thermometer at intervals of 0.5s, 1.0s, 2.0s, 4.0s, 8.0s, 15.0s, 30.0s, 60.0s, 120.0s, 240.0s, 480.0s and 1,440.0s. After 24 hours, the contents of the beaker were sieved through a No. 200 sieve (0.075 mm) and washed under running water. Six sieves with a mesh size smaller than 2.0 mm were used and shaken for 15 minutes. Following [12], 100g of the sample was taken to the oven to determine the hygroscopic humidity (w).

2.3. Preparing of Samples

First casted the samples containing only MgO e $MgSO_4$, (without limestone powder) called "Reference" (REF). Then started to incorporate 15%, 25%, 35% e 45%, in mass, to the "Reference" giving rise to samples "CALC15", "CALC25", "CALC35" e "CALC45" correspondingly (Table 3).

Table 3. Compositions of magnesium composite studied.

Sample	MgO (g)		$MgSO_4$ (g)		H_2O (L)		Salt concentration (g/L)	Limestone powder (g)		SW/P* Ratio
REF	844.86	54.55%	211.22	13.64%	0.4928	31,82%	428.6	0	0.00%	0.83
Calc15	611.74	46.36%	152.94	11.59%	0.3569	27,05%	428.6	197.92	15.00%	0.63
Calc25	586.71	40.91%	146.68	10.23%	0.3423	23,86%	428.6	358.54	25.00%	0.52
Calc35	549.16	35.45%	137.29	8.86%	0.3203	20,68%	428.6	542.12	35.00%	0.42
Calc 45	464.67	28.57%	139.40	8.57%	0.3253	20,00%	428.6	697.01	42.86%	0.40

(*) Ratio salty water/powder (MgO + limestone powder)

The order in which the materials were placed during preparation was:

1st) mix MgO and limestone powder (except REF sample),

2nd) salt dissolution $MgSO_4$ in water at 45°C using a salt concentration of 428,6 g/L,

3rd) homogenization of dry materials with salty water, and

4rd) samples casting.

The samples were casted following [13] and [14] (Using Portions of Prisms Broken in Flexure). Were casted 3 prismatic samples with width and height of 4 centimeters, and 16 centimeters of length, for each type of sample. Cure Process used was 28 days exposed to air in a laboratory environment.

To determine the expansibility of the composite, the procedure outlined in [15] was followed, molding specimens using the Le Chatelier Apparatus. Two specimens were molded for each sample. Subsequently, after molding and curing for 7 days immersed in water and lime, readings of the Le Chatelier needle openings were taken at two points: initially, after molding, and finally, after 7 days in the saturated state.

2.4. Tests performed

Prismatic samples (3 specimens for each type) were tested by standard [13] and [14] (using portions of prisms broken in flexural test) under laboratory ambient conditions (25 ± 5°C) (3 specimens for each type). Specimens of Le Chatelier Apparatus (determination of expandability) was tested by standard [15] (2 specimens for each type).

Flexural strength tests were performed using an Instron Universal Testing Machine, model 5982 and a 5 kN load cell. The distance between the lower supports adopted was 150 mm and the load application speed adopted was 2 mm/min (Figure 3a).

Dimensions specimens were determined with a digital caliper, Mitutoyo brand, with a precision of 0.01 mm, using the average of three measurements.

With the same specimens used in the flexural strength test, the [14] compressive strength test was carried out, whose standard recommends that portions of prisms broken in the previous test be used. Instron Universal Testing Machine model 5982 was used (Figure 3b).

(a) (b)

Figure 3. a) Flexural strength test made by ASTM C348–02 b) Compressive strength by ASTM C349-02

2.5. Microstructure analysis

Scanning Electron Microscopy (SEM) was used to study the microstructure of the samples by fractured surfaces. The equipment used was the Tescan VEGA 3 LMU of the Chemistry Institute of University Federal of Uberlandia. In microstructural observations, it was taken into account that the main hydration products that contribute to the MOS resistance is the 3·1·8 phase [$3Mg(OH)_2 \cdot MgSO_4 \cdot 8H_2O$] and 5-1-3 (or 5-1-2, since they have essentially the same structure) [$5\ Mg(OH)_2 \cdot MgSO_4 \cdot 3H_2O$]. By SEM of MOS, it is possible notice that phase 5-1-2 forms long needles, and phase 3-1-8 shows crystals that resemble scaly forms, and structures in the form of interlaced needles and their filling properties make 5-1-n phases preferred for increasing MOS strength in industrial applications [16].

III. RESULTS AND DISCUSSION

The unit mass determined for powdered limestone was 1.043 g/cm³ (1,043 kg/m³), the specific mass was 2.7272 g/cm³ (2,727.2 kg/m³), and the hygroscopic humidity was 0.51%.

Results of Sedimentation test are showed at Table 4 and granulometry distribution of limestone powder are showed at Table 5 and Figure 4.

Table 4. Sedimentation test of limestone powdered

t (min)	L (g/cm³)	z (cm)	T (°C)	μ 10E-6 (g.s/cm²)	Ld g/cm³	Qs	d (cm)
0.5	1.033	12.652	26	9.13	1.000738	73.29807	0.0638508
1	1.03	13.27	26	9.13	1.000738	66.48226	0.0462388
2	1.027	13.888	26	9.13	1.000738	59.66646	0.0334485
4	1.021	14.07688	26	9.0275	1.000738	46.03485	0.0288046
8	1.014	15.51888	26	9.0275	1.000738	30.13131	0.0213858
15	1.01	16.34288	26	9.0275	1.000738	21.04357	0.0160272
30	1.007	16.96088	26	9,0275	1.000738	14.22776	0.0115452
60	1.005	17.37288	26	9.1517	1.000738	9.683895	0.0082623
120	1.004	17.57888	26.5	9.1103	1.000466	8.029103	0.0058768
240	1.003	17.78488	26.5	8.924	1.000466	5.757168	0.0041798
480	1.002	17.99088	27	8.8205	1.000188	4.116064	0.0029727
1440	1.002	17.99088	26	9.13	1.000738	2.86809	0.0017163

Where: t= time; L= density; z= particle drop height; T= temperature; μ= viscosity coefficient; Ld= densimeter reading; Qs= percentage of soil in suspension; d= maximum particle diameter.

Table 5. Granulometry distribution of limestone powder

	Percentage pass (%)	Diameter (mm)
Coarse sieving	100	19
	100	9.5
	100	4.8
	100	2
Fine sieving	100	1.2
	99.985	0.6
	99.971	0.42
	99.759	0.25
	98.500	0.15
	90.914	0.075
Sedimentation	90.914	0.063850771
	38.653	0.046238849
	37.313	0.033448482
	33.963	0.02880465
	31.283	0.021385755
	29.274	0.016027215
	27.904	0.01154524
	25.164	0.008262276
	11.826	0.005876847

	2.569	0.004179836
	2.789	0.002972658
	2.269	0.001716265

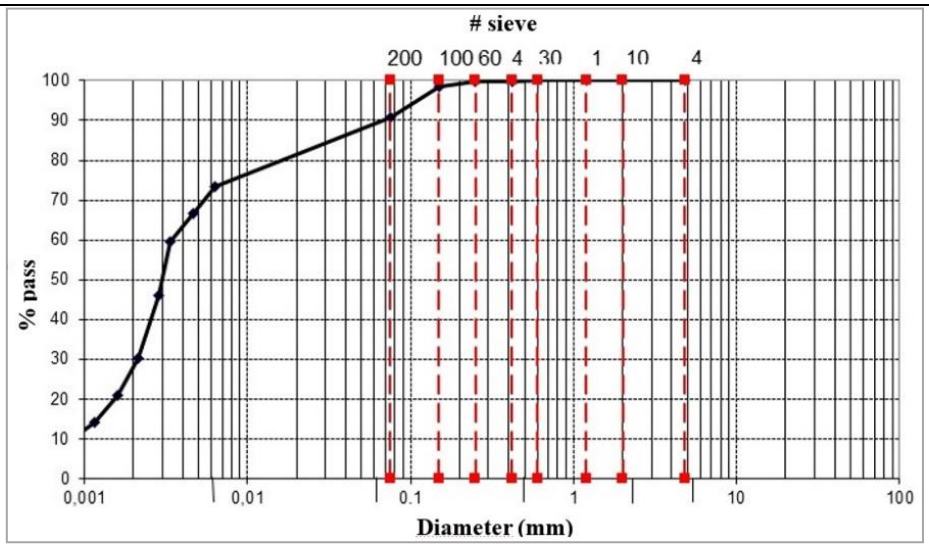


Figure 4. Granulometry distribution of limestone powder

From granulometry distribution curves it was concluded that the material is extremely thin, about 75% < 0.006mm.

Table 6 and Figure 5 (a and b) show the results obtained from flexural strength and Compressive strength tests varying the limestone powder proportion in the mix.

Table 6. Flexural strength and Compressive strength tests results

Sample		Flexural strength (MPa)	Deviation	Compressive Strength (MPa)	Deviation
REF	1	1.51	0.10	18.2	2.4
	2	1.46		13.5	
	3	1.63		14.7	
	M	**1.53**		**15.5**	
CALC15	1	1.46	0.14	17.9	0.1
	2	1.34		18.0	
	3	1.29		18.1	
	M	**1.36**		**18.0**	
CALC25	1	1.65	0.16	17.4	1.1
	2	1.48		16.7	
	3	1.85		18.9	
	M	**1.66**		**17.7**	
CALC35	1	2.50	0.31	17.4	1.4
	2	2.05		19.8	
	3	2.20		19.9	
	M	**2.25**		**19.0**	
CALC45	1	2.02	0.73	14.3	1.4
	2	3.79		13.5	

	3	2.62	16.3
	M	**2.81**	**14.7**

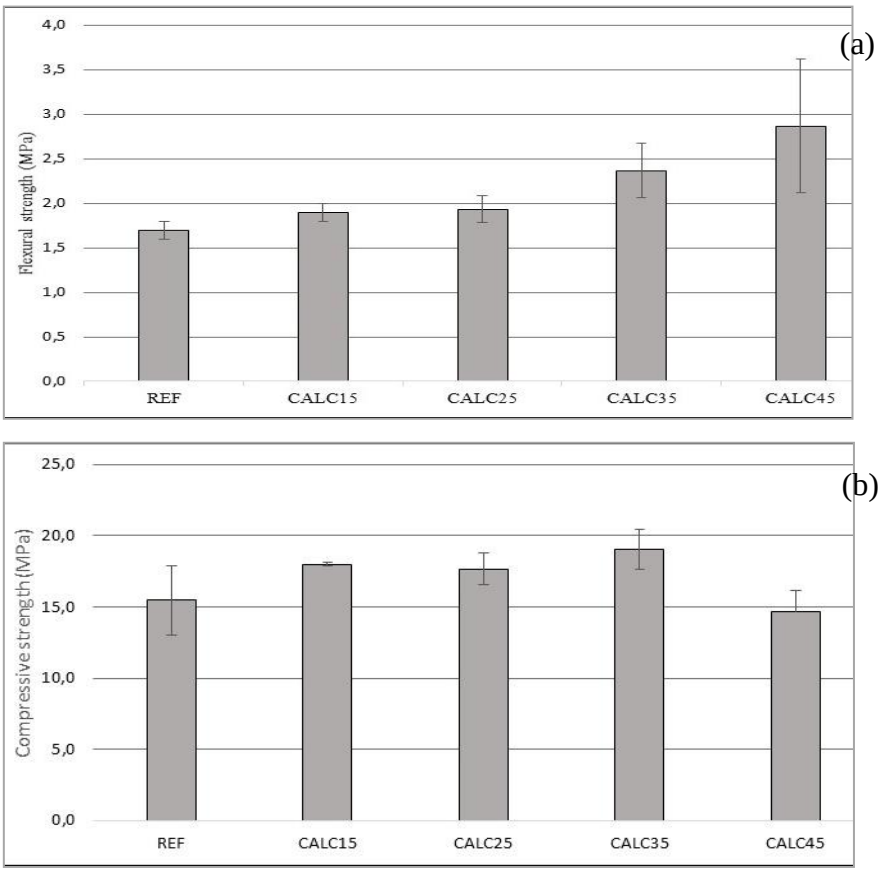


Figure 5. a) Flexural strength tests results b) Compressive strength tests results

It was verified that there was a continuous increase in the flexural strength as the incorporation of limestone powder in the mixture is increased. The best result obtained was in the sample with the highest limestone index (CALC45), representing an increase of about 70% in the flexural strength regarding to the sample without limestone (REF), although the tests carried out on the specimens of the CALC45 sample have shown a deviation above those obtained in the others.

Different from the results obtained in flexural strength, it was verified that the compressive strength did not show a linear behavior, indicating that there is a gain in compressive strength in the incorporation of limestone powder in the mixture in the range between 15% and 35%, accompanied by a relative constancy around 18 MPa. The samples with 45% limestone shows a drop in strength and lower values than the REF.

Table 7 shows the Expandability test from Le Chatelier Apparatus, varying the limestone powder proportion in the mix.

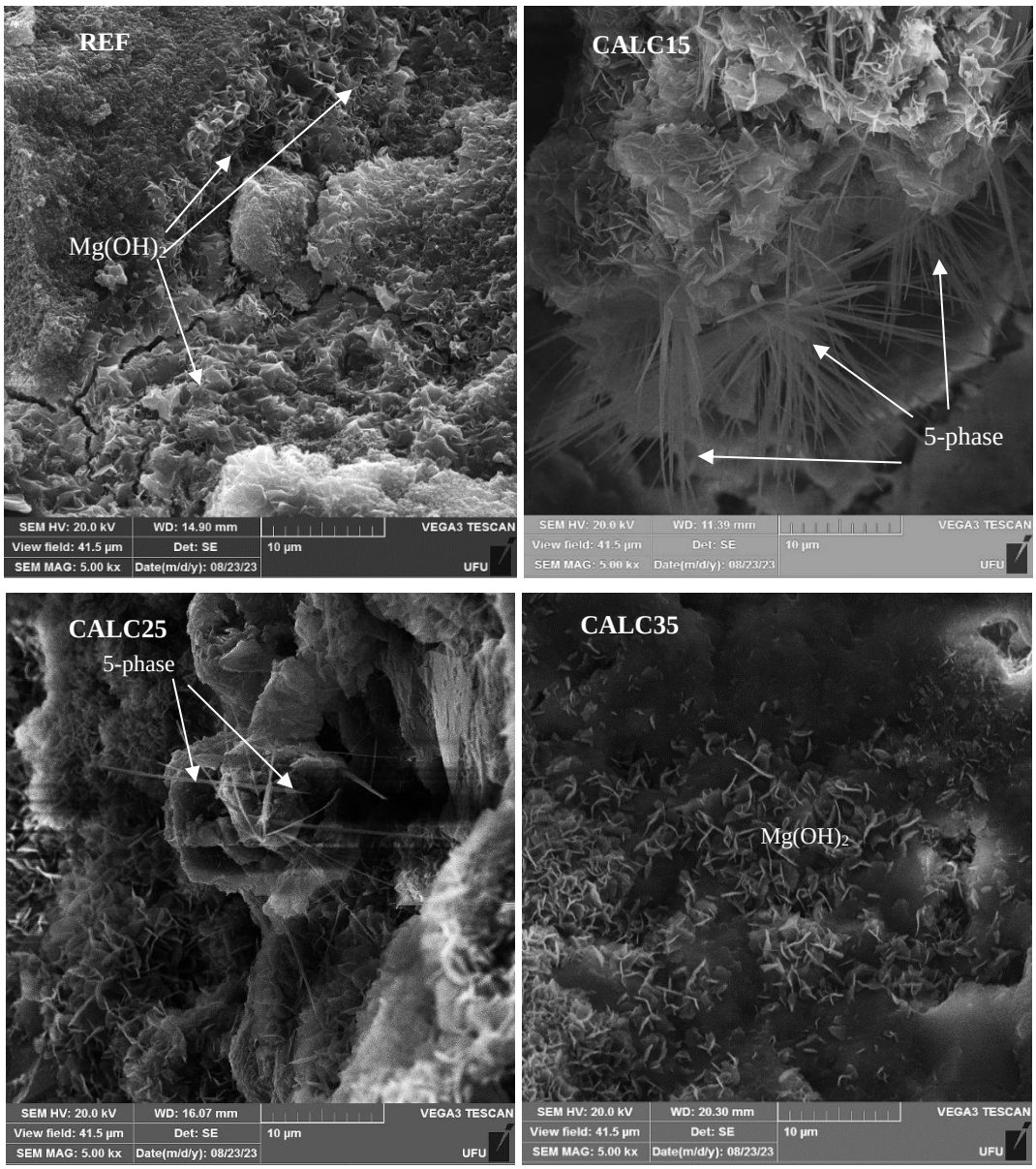
Table 7. Expandability test from Le Chatelier Apparatus results

Sample		Initial open (mm)	Final open (mm)	Difference (mm)	Expansion (E) or Retraction (R)
REF	A	0	0.81	0.81	E
	B	0	0.32	0.32	E

CALC15	A	0.97	1.91	0.94	E
	B	0	0	0	-
CALC25	A	0	0.63	0.63	E
	B	0	0.04	0.04	E
CALC35	A	3.73	3.15	-0.58	R
	B	5.57	6.59	1.02	E
CALC45	A	4.44	3.57	-0.87	R
	B	2.13	2.11	-0.02	R

From the analysis of the test, it is verified that, as the carbonate material is added to the composite, there is a decrease in the expandability of the samples since it is an inert material, while MgO has a tendency to expand during its reaction. When the carbonate material is added at 35%, there is a more pronounced retraction.

Microstructural analysis by SEM was showed by Figure 6.



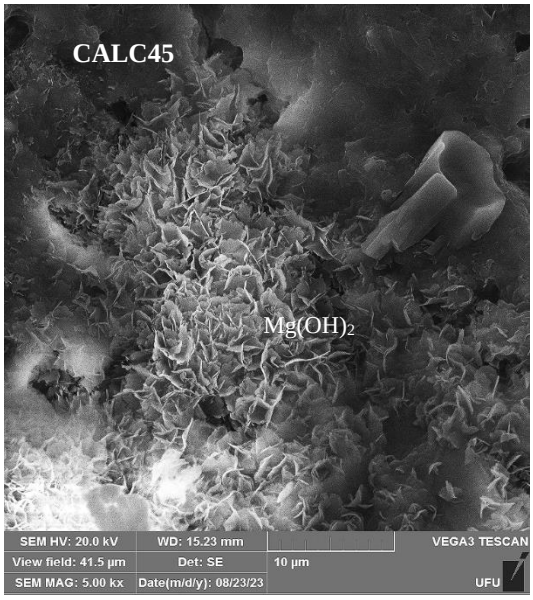


Figure 6 – Images of the microstructure by SEM of samples REF, CALC15, CALC25, CALC35 and CALC45

IV. CONCLUSION

Through this study, it is indicated that the incorporation of limestone powder in the mixture can be beneficial in relation to the resistance gain, both to flexion and compression. It was found that the greater the incorporation of limestone powder in the mixture, the greater the flexural strength, with its best result being obtained in the sample with the highest proportion of limestone in the study, with 45% (CALC45). However, for the compressive strength, it was verified that the mixtures show gains in the range of incorporation of carbonate material from 15% to 35% and, from there, a drop in strength, since CALC45 presented lower results than the trace without limestone (REF).

Therefore, aiming at optimizing both flexural and compressive strength, the best result obtained was the sample with the incorporation of 35% limestone powder (CALC35). Future research carried out between addition levels varying between 35% and 45% will possibly show what is the value at which the inflection occurs in the limestone addition versus compressive strength curve.

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