Mortar Based on Sludge from Carbonate Dimension Stone Processing Industry - an Experimental and Feasibility Approach

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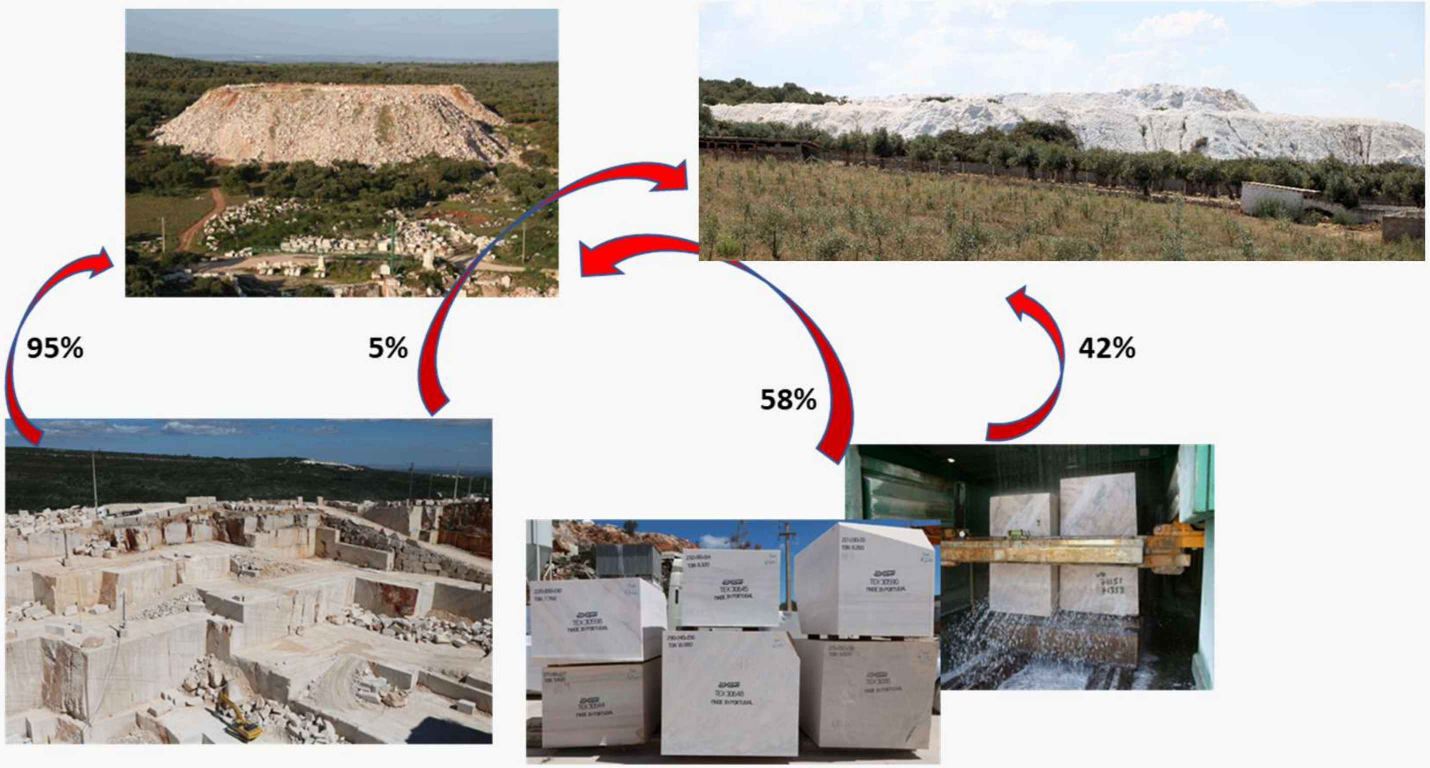
1. Introduction

The carbonate dimension stone extractive and processing industry produces large amounts of wastes later deposited in heaps and deposits of carbonate sludge.

The waste and residues are basically divided into two types:

1 – In quarries:
i) Rock fragments that contribute with around 95%;
ii) Carbonated sludge with 5% contribution.

2 – In processing units:
i) Rock fragments - 58%;
ii) Carbonated sludge - 42%.



Environmental impacts are inevitable, the main ones being:

- reduction of vegetation cover;
- decrease in agricultural activity;
- soil sealing;
- alteration of water lines with a significant reduction in its quality;
- alteration of ecosystems;
- decrease in air quality;
- reduction in the photosynthetic process of plants;
- visual impact.

Carbonate sludge is considered waste because it has not yet been used industrially to give it an economic value. However, they have high degrees of purity and relevant physical and chemical characteristics that make them materials with high potential for use in various industries, especially those that include calcium carbonate ($CaCO_3$) in their production processes.

2. Objectives

The Geosciences Department at the University of Évora, has a line of research that studies the potential of these wastes as raw materials in other industrial applications.

The Calcinata project (Project for I&dt Companies in Co-promotion, with reference nº 72239 co-financed by Alentejo 2020, Portugal 2020 and the European Union through the "European Regional Development Fund (FEDER)") is the most recent project in this scope which explore this potential.

Calcinata research project proposed to study the application of carbonated sludge from the processing of marble and limestone, as an integral part of resinous binders, later incorporated into stone composites.

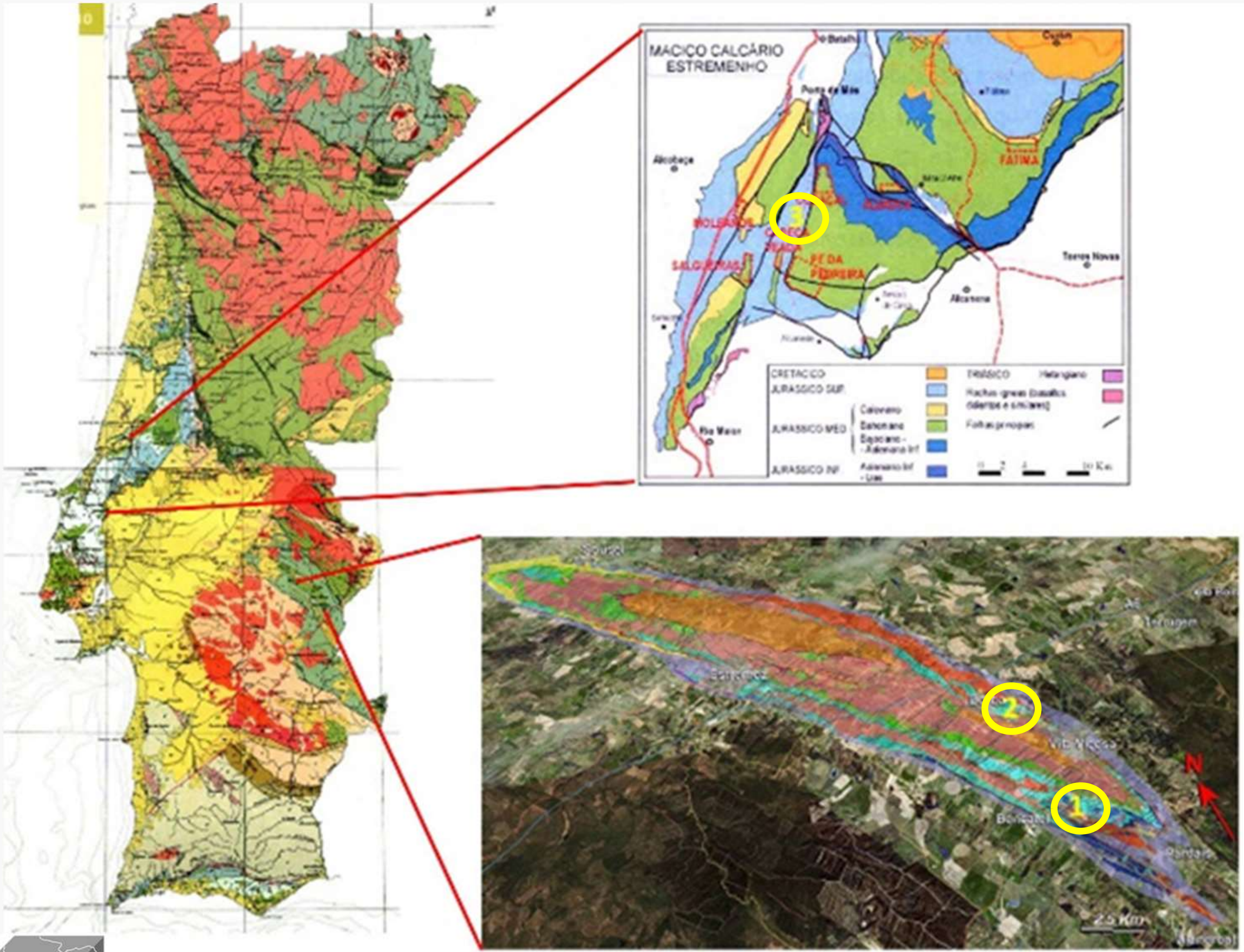
2. Materials and Methods

2.1. Geographic Location

A sampling campaign was carried out in the Marbles Area (MA) and in the Limestones Area *(LA)*.

	Lisbon	Porto	Algarve
Marbles Area (MA)	150 km	270 km	190 km
Limestone Area (LA)	130 km	190 km	340 km

2.2. Geological Setting



Sampling location on a geological basis took place:

- Estremoz Anticline; is an elliptical-shaped geological structure, about 42 km long and 8 km wide, NW-SE orientation. / Estremoz Carbonated Sedimentary Volcanic Complex; Paleozoic calcitic marbles:

1 – Carbonate sludge from *Texugo* quarry (*António Galego & Filhos Company*).

2 – Carbonate sludge from the JPL quarry (*Marmetal / A.L.A. Almeida Companies*).

- Estremenho Limestone Massif; Area with 800 km^2 consisting of Jurassic limestones with about 160 million years:

3 – Carbonate sludge from Cabeça Veada quarry (*Solancis* and *MVC Companies*).

2.3. Sampling

Limestone Carbonated Sludge

Solancis - Sociedade Exploradora de Pedreiras SA, referenced as **C(S)**.

MVC - Mármores de Alcobaça Lda., referenced as **C(MVC).**

Sampling carried out at the processing units and at the exit of the filter press of the industrial water treatment units, thus preventing contamination of the carbonated sludge.

Marble Carbonated sludge

António Galego & Filhos – Mármores SA, referred to as **M(AGF).**

A.L.A. de Almeida SA., referred to as **M(A).**

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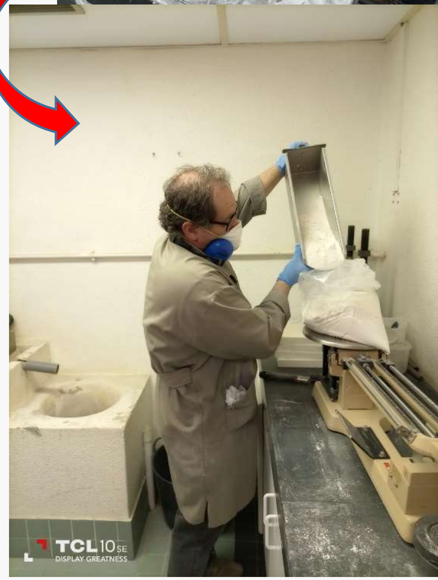
2.4. Sample Preparation

Manual disaggregation

Drying at room temperature

Mechanical disaggregation in jaw mill

Bagging in 5 kg bags



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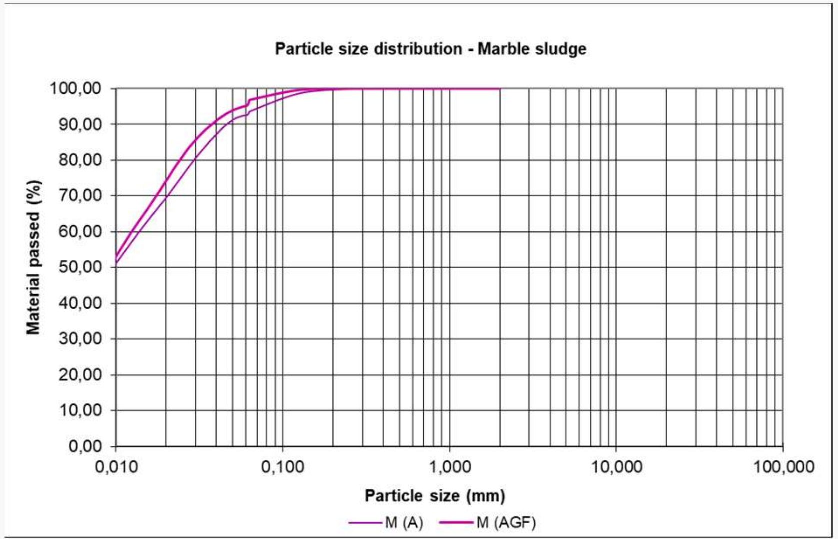
3. Carbonate sludge characterization and Results

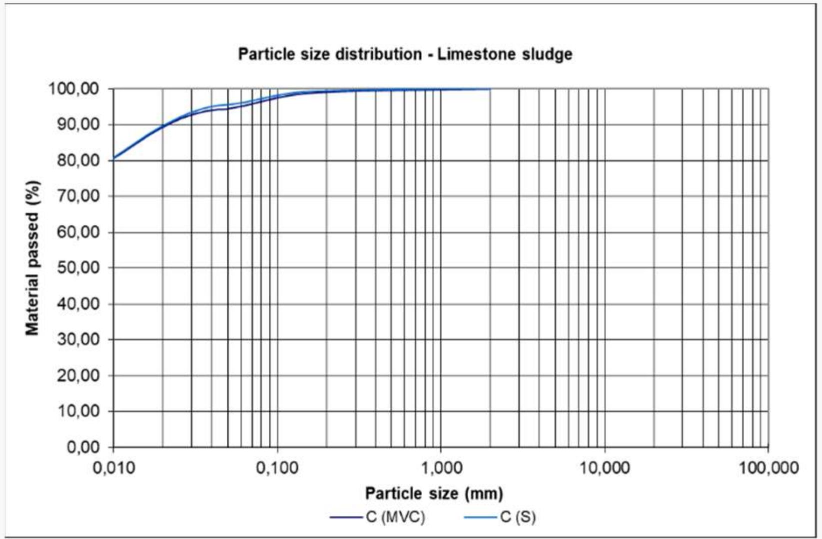
3.1. Physical Characterization of the Carbonate Sludge

- The particle size distribution

The particle size distribution of the constituent was obtained by combining the analyzes of the fraction composed by particles with equivalent spherical diameter (e.s.d) > 0.063 mm and the fraction composed by particles with equivalent spherical diameter (e.s.d) < 0.063 mm.

Similar granulometric curves between the two limestone samples and the two marble samples. Limestone muds are slightly finer than marble muds.





- Density of the carbonate sludge

Density was determined according to the pycnometer method revealed the following results:

M(A) – 2.537 g/cm^3
M(AGF) – 2.559 g/cm^3
C(S) – 2.490 g/cm^3
C(MVC) – 2.493 g/cm^3.

3.2. Chemical Characterization of the Carbonate Sludge

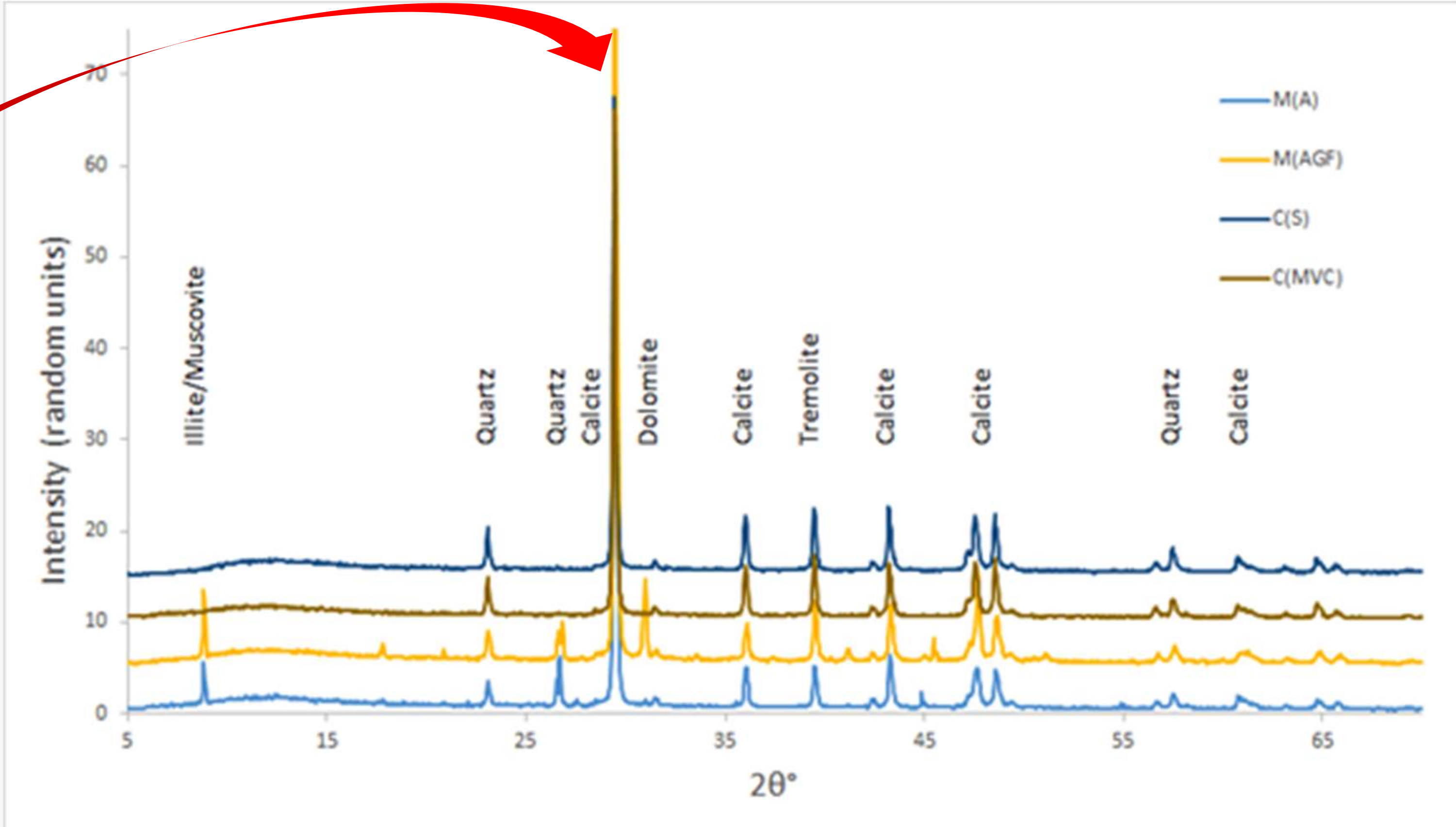
- Loss on Ignition;
- Contents of the following major elements: Mn, Ti, Ca, K, Si, Al, Mg, Na and Fe, expressed in percentage as oxides: MnO, TiO_2, CaO, K_2O, SiO_2, Al_2O_3, MgO, Na_2O and Fe_2O_3

Samples	Al_2O_3	SiO_2	CaO	MgO	Fe_2O_3	K_2O	Na_2O	MnO	TiO_2	Loss on Ignition (%)
M(AGF)	0.545	2.549	45.504	3.156	0.228	0.253	0.564	0.030	0.017	42,97
C(MVC)	0.278	0.357	52.580	0.337	0.089	0.092	0.583	0.004	0.006	43,50
C(S)	0.276	0.297	54.189	0.301	0.089	0.143	0.620	0.004	0.011	43,30
M(A)	0.716	3.537	51.555	0.829	0.274	0.362	0.670	0.008	0.026	42,15

All carbonated sludges have significant percentages of **CaO** and in the **loss of ignition test**. M(AGF) and M(A) expressed in $\boldsymbol{SiO_2}$ and M(AGF) something magnesium (**MgO**).

3.3. Mineralogical Composition of Carbonate Sludge

M(A), M(AGF), C(S) and C(MVC) markedly carbonated muds, with well-defined x-ray diffraction peaks in Calcite.



4. Formulations

Constitution of formulations with different percentage contributions of carbonate sludge and polyester resin, branded Recapoli 2196.

Mortar Formulations	NM (Marble Sludge)	NC (Limstone Sludge)	Resine (Polyester)
ANM3	54,43%		45,57%
ANM4	50%		50%
ANM5	47%		53%
ANM6	52%		48€
ANC3		52,31%	47,69%
ANC4		50%	50%
ANC5		47%	53%

Why Polyester?

Transparent polyester resin with UV filter to prevent yellowing. Ideal for pouring over a silicone mold in the manufacture of highly transparent decorative pieces, models, prototypes, etc.

Why not Epoxy?

Resoltech 1050 (Epoxy) - 665€ / 25 kg; £758,10 / 25 kg

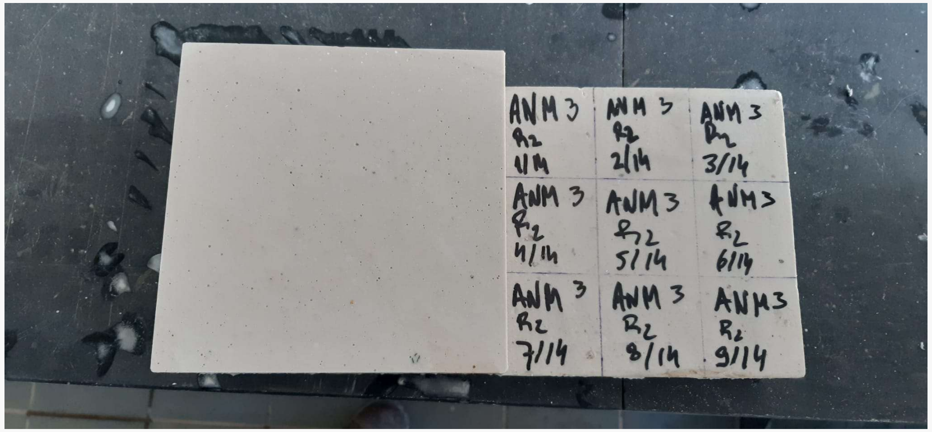
Recapoli 2196 (Polyester) - 169€ / 25kg; £192,66 / 25 kg

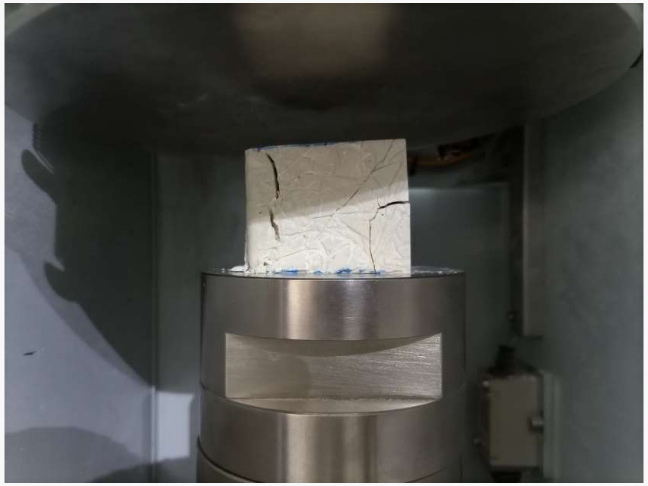
4.1. Preparing the Formulations

Moulds (15 cm x 15 cm x 15 cm) filled with the mixtures of binder with limestone and marble sludges and polyester resin.

After demolding the cubes were cut into 5 cm x 5 cm x 5 cm specimens, for determination of the compressive strength.

4.2. Mechanical Characterization of Binders





After demolding, the specimens kept for curing in air and were evaluated at 7, 14 and 28 days, with increasing uniaxial compressive strength over this period, reaching higher uniaxial compression values at 28 days.

Formulations %	R (MPa)
ANM3 – 54,43%NM / 45,57%Res.	102.73
ANM4 – 50%NM / 50%Res.	98.35
ANM5 – 47%NM / 53%Res.	96.23
ANM6 – 52%NM / 48%Res.	106.37 ←
ANC3 – 52,31%NC / 47,69%Res.	103.20
ANC4 – 50%NC / 50%Res.	102.12
ANC5 – 47%NC / 53%Res.	96.04

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5. Conclusions

- At a proportion of 52% carbonated sludge and 48% resin, the formulation with marble carbonated sludge showed an increase of 3MPa in compression strength when compared to limestone, these two having shown the best performances in terms of mechanical compression strength.
- Achieved results revealed the possibility of substituting epoxy resins for polyester resins, reflecting the economic advantage in the prices of the final products.

6. Latest Studies

- Formulation of different compositions integrating aggregates from marble crushing, with different granulometry, thus constituting more environmentally sustainable stone composites.

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