APPLICATION OF RESINOUS BINDERS WITH INCORPORATION OF CARBONATED SLUDGES from the dimension stone industry in the production of stone composites

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Summary: *The main objective of the Calcinata Project - Production of lime-based mortar from the calcination of carbonated sludge from the ornamental stone industry (marbles and limestone), was to present an alternative use for waste (slurries) from cutting and polishing carbonated ornamental rocks . The industrial application of this waste makes it possible to add value, transforming it into a by-product, thus contributing to the framing of the limestone and marble extractive and processing sub-sectors, in the "Action Plan for the Circular Economy", promoting the sustainable growth. This research showed that recycling slurries has relevant potential since they can be used as a raw material integrated in binders production used in the manufacture of ornamental stone composites materials partial or totally replacing the epoxy resins traditionally used in this type of products.*

Key words: *sludge, marble, limestone, binder, composites*

1. Introduction

The carbonated dimension stone extractive and processing industry produce high amounts of wastes that are deposited in the open in heaps and deposits of carbonated sludge (Fig. 1).

Environmental impacts are unavoidable, such as: i) reduction of vegetation cover, ii) decrease in agricultural activity, iii) soil sealing, iv) alteration of water lines with a significant reduction in its quality, v) alteration of ecosystems, vi) decrease in air quality, vii) reduction in the photosynthetic process of plants and visual impact, the latter being quite striking, as the white color of the deposits is very contrasting with the mainly rural surrounding environment (Afonso et al, 2023).

The industrial application of this waste makes it possible to add value, transforming it into a by-product, thus contributing to the framing of the limestone and marble extractive and processing sub-sectors, in the "Action Plan for the Circular Economy", promoting the sustainable growth. By this means, this research has shown that the recycling slurries as a raw material are possible to integrate binders production through its incorporation on the manufacture of ornamental stone composite materials, partial or totally replacing the epoxy resins traditionally used in this type of products.

Fig. 1 Deposit of carbonated sludge close to Vila Viçosa village.

2. Materials and Methods

The slurries were sampled in the filter presses plants at the companies: *António Galego & Filhos – Mármores SA*, referred to as M(AGF) and *A.L.A. de Almeida SA*, referred to as M(A). The limestone carbonated sludge was collected at *Solancis - Sociedade Exploradora de Pedreiras SA*, referenced as C(S) (Fig. 2) and *MVC - Mármores de Alcobaça Lda.*, referenced as C(MVC).

The laboratory work on the physical, chemical and mineralogical characterization of the slurries was carried out at the laboratories of the University of Évora, namely Geosciences Department, Mechanical Testing, Hercules and Ambiterra laboratories.

Fig. 2 Sampling of ilmestone carbonated sludge in Solancis factory.

After the slurry's characterization phase, a new stage began with binder formulations composed with different percentages of sludge and polyester resin, Recapoli 2196 by the Castro Composites Company, and consequent physical-mechanical evaluation at three curing times: 7, 14 and 28 days.

Once the best performing binder formulation has been determined, composites were prepared using marble aggregates supplied by *Marvisa, Mármores Alentejanos Lda.* Company. The mixture of the binders and aggregates were mixed and poured into 55 cm x 15 cm x 15 cm moulds to produce specimens' for subsequent stone composite physical-mechanical characterization.

3. Sludges - Physical and Chemical Characterization

Among the physical and chemical characterization, granulometric analysis (through particle sieving and sedigraph methods) and chemical and mineralogical composition of the samples stand out. From the point of view of granulometric distribution, the samples of limestone and marbled sludge showed similar distributions with the particularity of the limestone sludge having a finer granulometry than the marbled sludge, as shown in Figure 3.

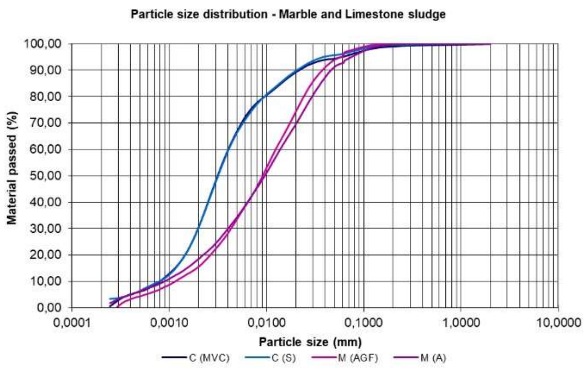

Fig. 3 Particle size distribution on the selected marble and limestone sludge samples.

The chemical analyses carried out using atomic spectrometry revealed a fundamentally carbonated material. All carbonated sludges have significant percentages of CaO and show relevant percentage of loss of ignition. M(AGF) and M(A) depicted small percentage of SiO_2 (2.5 – 3.5%) and M(AGF) show the presence of magnesium (MgO) (Table 1).

Table 1 – Chemical analysis.

Samples	CaO (%)	SiO_2 (%)	MgO (%)	Loss on Ignition (%)
M(AGF)	45,504	2,549	3,156	42,97
M(A)	51,555	3,537	0,829	42,15
C(MVC)	52,580	0,357	0,337	43,50
C(S)	54,189	0,297	0,301	43,30

Mineralogical analysis corroborated the carbonate character of the sludges, with a well-defined peak in calcite on x-ray diffraction.

4. Formulation of Binders Consisting of Carbonated Sludge and Resin

Formulations were made with different percentage contributions of marbled sludge and polyester resin, the same being done with limestone sludge. The characterization was carried out at different times:

i. Preliminary tests with manual mixtures in order to visually observe the final products after drying;
ii. Physical characterization based on the viscosities studied from the formulations made only with manual mixtures;
iii. Mechanical characterization based on tests of mechanical resistance to compression of cubic specimens, obtained from formulations prepared into molds measuring 15 cm x 15 cm x 15 cm.

For the evaluation of viscosity, an innovative experimental methodology was developed that allowed to perform a comparative evaluation on the viscous behavior of different binders. This methodology is based on an experimental device (Fig. 4) consisting of a glass plate that is positioned at a 45° inclination, to which a metal ruler is associated that allows measuring the displacement of the binder through time. In this way, it is possible to assess the fluidity of the binder when it is placed on the glass.

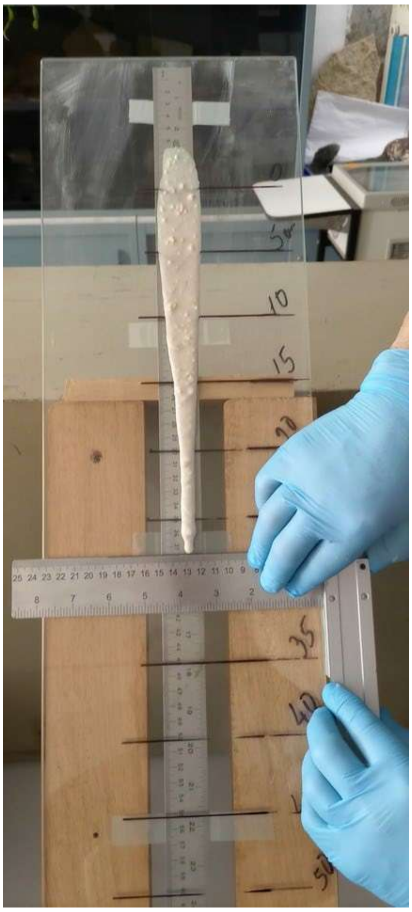

Fig. 4 Experimental set-up for viscosity and rheological measurments

To carry out this test, times were pre-established for: i) mixing the resin with the conditioner; ii) filling an adapted syringe and iii) emptying it at the top of the set-up ramp. After this, sliding times were measured.

Figure 5 shows the viscosity graphic representation of the four formulations with limestone sludge and another four with marble sludge. The fractional number represents the percentage of sludge in the numerator and the percentage of polyester resin in the denominator.

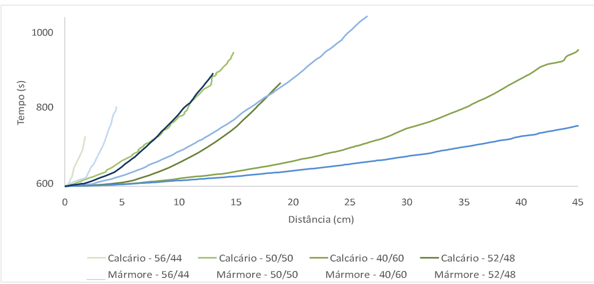

Fig. 5 Viscosity graphic representation of binder formulations.

Analyzing the graph from Fig.5, identical behavior can be observed for the formulations with the same percentages of sludge and resin. The higher the percentage of resin, the more fluid the binder becomes. The aim of this research being to reduce resin and increase the contribution of sludge.

The mechanical characterization of the binder was carried out by evaluating the resistance to uniaxial compression of the different formulations with different percentage contributions of limestone and marble sludge and resin. The tests were carried out on cubic specimens with a 5 cm side and using a Pegasil compression press. After demolding, the specimens kept for curing in air and were tested at 7, 14 and 28 days, with increasing uniaxial compressive strength over this period, reaching higher uniaxial compression values at 28 days. Test were made according to the NP EN 1926:2008 standard. These results are shown in Table 2 (Afonso, P. et al, 2023).

Table 2: Results of uniaxial compressive strength tests after 28 days of curing.

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

NM – Marble sludge; NC – Limestone sludge; Res – Resine.

The 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 binders showed the best performances in terms of mechanical compression strength. The results obtained in the tests carried out allowed us to establish the ideal binder, with a proportion of 52% sludge (limestone / marble) and 48% polyester resin.

5. Composite Formulations with Binder 52/48 and Marble Aggregates

With the formulation of stone composites, it was intended to obtain prototypes with different compositions of aggregate and binder 52/48 (Table 3). The marble aggregate, supplied by the company *Marvisa, Mármores Alentejanos Lda.*, consisted of three types, referred to as BA, B1 and B2, with the following granulometric intervals: BA (4 mm / 6.3 mm), B1 (8 mm / 14 mm) and B2 (14 mm / 25 mm).

Table 3: Stone composite formulations.

Formul.	**Aggregates**			**Binders**		
	BA	**B1**	**B2**	**NC**	**NM**	**Res**
F1	30%	30%	40%	52%		48%
F2	20%	20%	60%	52%		48%
F3	35%	15%	50%	52%		48%
F4	40%	40%	20%	52%		48%
F5	30%	30%	40%			52
F6	20%	20%	60%			52
F7	35%	15%	50%			52
F8	40%	40%	20%			52

Using a light mechanical mixer, the binder was mixed (sludge / resin + catalyst), subsequently introducing the aggregates (Fig. 6). After the period necessary to ensure complete homogenization of the entire mixture, it was poured into metal molds measuring 15 cm x 15 cm x 15 cm and 55 cm x 15 cm x 15 cm, with a view to obtaining specimens for different characterization tests. Adopting the same criteria used in the study of the binders, the objective was to study the specimens with three curing times: 7, 14 and 28 days.

After the uniaxial compressive strength tests (NP EN 1926-2008) in specimens subject to the three curing times, strength results were obtained in the specimens tested at 28 days (Table 4).

By analyzing the data, it can be seen that the formulation made up of F(4) limestone sludge and 52% Aggregates (40%BA/40%B1/20%B2) + 48% Binder (52%limestone sludgel+48% Resin) was the one that presented the best results, reaching 91.96 MPa. The best formulation with marble sludge was F8 with 88.19 MPa.

Having defined the formulations with the best performance, in terms of compression strength, the remaining characterization tests were made, namely: i) determination of flexural strength under concentrated load (Table 5); ii) apparent density and porosity (NP EN 1936-2008) (Table 6); iii) absorption of water at atmospheric pressure (NP EN 13755) (Table 7) and iv) absorption of water by capillarity (NP En 1925-2000) (Table 8).

Fig. 6 Stone composites formulation mixing and vibration in the mold.

Table 4: Uniaxial compressive strength test results for the several formulations.

Formulations	**Average uniaxial Compression Strength (MPa)**
F1	73.30
F2	69.06
F3	61.11
F4	**91.96**
F5	52.26
F6	76.33
F7	81.20
F8	**88.19**

The specimens for the flexural strength test were obtained from the block produced in the 55 cm long molds, thus allowing them to have the dimensions of 30 cm x 5 cm x 5 cm (Fig. 7), required by the NP EN standard 12372.

Fig. 7 Specimens obtained from cutting the block with a marble sludge binder.

Table 5: Flexural strength.

Curing (Days)	Binder	Flexural strength (MPa)
28	Marble	1549 ± 1.38
	Limestone	13,49 ± 0.97

Table 6: Apparent density and open porosity.

Binder	Volume of open pores (ml)	Apparent volume (ml)
Marble	0.22 ± 0.03	117.0 ± 7.0
Limestone	0.21 ± 0.04	104.6 ± 7.4
Binder	**Apparent density (g/m³)**	**Open porosity (%)**
Marble	2.279 ± 0.014	0.19 ± 0.02
Limestone	2.263 ± 0.017	0.20 ± 0.03

Table 7: Water absorption at atmospheric pressure.

Binder	Water absorption at atmospheric pressure **(%)**
Marble	0.2 ± 0.03
Limestone	0.1 ± 0.03

Table 8: Water absorption through capilarity.

Binder	Average (g/m².s)
Marble	0.088 ± 0.010
Limestone	0.062 ± 0.019

6. Future Works

To better characterize the formulations, freeze-thaw tests will be carried out at the Mechanic Testing Laboratory (LEM), according to Standard NP EN 012371_2015 and using a FitoTerm-700GD25 climatic chamber, repeating the tests. The following tests on polished specimens will also be considered: thermal shock, brightness, roughness and color.

7. Conclusions

Atendendo aos resultados obtidos conclui-se o seguinte:

In view of the results, the following is concluded:

1 – The use of polyester resin in replacement of epoxy resin seems feasible. The price of epoxy resin is on average four times higher than polyester resin, which makes stone composite products substantially more expensive.

2 – As one goal of the investigation was the reduction of resin and its partial replacement by carbonated sludge, the investigation gradually incorporated successively higher percentages of solid load, without compromising the strength of the specimens. Thus, the ideal binder percentage was: 52% carbonated sludge and 48% polyester resin.

In the formulations with marble aggregate, the ideal percentage was achieved with 52% of aggregate and 48% of binder, which leads to a substantial reduction of resin in the formulation of a stone composite.

3 – The results obtained in the compressive and flexural strength tests are promising, given the fact that the formulations were carried out manually using a manual mixer. Execution in an industrial context using a suitable mixer with a vacuum chamber will allow a more homogeneous product, with expected higher density and without structural defects, allowing improved values of compression and flexural strength.

3.1 - A comparison with values of mechanical compression strength, traditionally found in different lithotypes sold as ornamental rock, considering the lowest and highest values of each stone type (Catalogue of Portuguese Ornamental Stones) show that the developed stone composites are within an equivalent range of performance:

Limestones: Pedra de Ançã (23 MPa) – Banco de Baixo (167 MPa).

Marbles: Rosa Venado (70 MPa) – Branco Venado (102 MPa).

Granites: Amarelo Vila Real (70 MPa) – Cinzento Alpalhão (253 MPa).

Recalling the highest values obtained in the compressive strength tests on formulations (F4 – 91.96 MPa; F8 – 88.19 MPa), it can be concluded that they are within the range of values for natural stone.

3.2 - Regarding flexural strength, to establish a comparison with different lithotypes marketed as ornamental rock, the example of some reference values is given (Catalog of Portuguese Ornamental Rocks):

Limestones: Olho de Sapo (Arrimal) (9 MPa) – Branco do Mar (31 MPa).

Marbles: Rosa (15 MPa) – Creme Venado (29 MPa).

Granites: Amarelo Figueira (6 MPa) – Azulália (35 MPa).

Similarly, to compression strength, flexural strength are also within the range of a large part of natural dimension stones.

4 – With regard to water absorption at atmospheric pressure, natural stone vary between: i) 0.2% and 9.6% on limestones; ii) 0.2% and 1.05% on granites and around 0.1%on marbles. The stone composites are also within this range of absorption values.

5 – Regarding open porosity, the two stone composites present values of approximately 0.2%, equivalent to the open porosities detected in marbles. Composites open porosity is lower than the one usually seen in granites (0.4%, 0.7%) and limestones (0.4%, > 1%) according to the Portuguese Ornamental Stones Portal, LNEG.

6 – Despite the studies not yet being completed, the possibility of using polyester resin in stone composites is very promising, as well as the incorporation of carbonated sludge from the processing of limestone and marble, thus contributing to the reduction of environmental impacts caused by the accumulation of these materials in the open.

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