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

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Abstract

The extractive and processing of carbonate dimension stone, such as limestone and marble is particularly important in Portugal. The main extractive centres are in the marble triangle formed by Estremoz, Borba, Vila Viçosa and also the Estremenho Limestone Massif. The large number of quarries and processing units, given the techniques used, both in extraction and processing, and the high-quality criteria required for final ornamental stone products, inevitably lead to the production of stone waste and carbonate sludge. The Geosciences Department at the University of Évora, has a research programme that studies the potential of these wastes as raw materials in other industrial applications. The Calcinata project is the most recent project in this scope which explores this potential. Carbonate sludge has relevant physical and chemical characteristics, which means that they have a strong binding capacity with aggregates, thus allowing their use as a raw material in mortars that can later be used to produce more sustainable composites of stone origin. This research is focused on the study of more sustainable natural stone composite materials that will help to decrease the threatens to natural environment by reducind the amount of carbonate sludges deposited in opend fields and the related geohazards. This work clearly opens a field of investigation regarding the circular use of the natural stone extractive industry residues pointing to innovative solutions for carbonate sludges with obvious positive environmental impacts.

Keywords: Carbonate sludge, ornamental stone, marble, limestone, composites.

1. Introduction

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

Environmental impacts are unavoidable, such as: 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 and visual impact, the latter being quite striking, as the white colour of the deposits is very contrasting with the mainly rural surrounding environment (Figure 1) (Martins, 1997; Ventura et. Al., 2009).

In the extractive units, this waste and residues result from the production cycle, fundamentally from drilling, cutting and excavation operations. The low yield in this subsector, particularly in the marble area in *Alentejo* located in the south of Portugal, is largely due to the geological characteristics of the massif, mainly the high degree of fracturing. Placing the productive yield of the quarries in a range between 10% and 30%, meaning that the rest of the excavated material will inevitably feed heaps in addition to the deposits of carbonate sludge. These waste and residues are basically divided into two types: i) rock fragments that contribute with around 95%; and ii) carbonate sludge with 5% contribution. In the processing plants, the waste comes from operations associated with cutting processes and surface treatment, namely polishing slabs and tiles. In the processing subsector, sawmills are responsible for producing 30% of waste in processes related to cutting natural stone blocks for their division into slabs and 30% in other surface cutting and finishing operations. Of the total waste produced by sawmills, it is estimated that around 58% correspond to rock fragments and 42% to carbonate sludge.

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. The scientific and technological proof of the characteristics of carbonated sludges give them the possibility, or ability to be incorporated into other industrial processes, thus allowing their classification as by-products of the extractive and processing industry of carbonate dimension stones.

Calcinata research project proposed to study the application of carbonate sludge from the processing of marble and limestone, as an integral part of resinous binders, later incorporated into stone composites. Currently these composites are industrially produced using epoxy resins which is a thermosetting polymer that hardens when mixed with a catalyst or curing agent, presenting an intense smell, being still reactive to heat. The risk associated with the use of this type of material essentially has to do with the application of the amine hardener, which can be corrosive and toxic or even carcinogenic. When applied to exterior cladding materials, epoxy resins are subjected to UV radiation from sunlight and to chemical reactions with consequent degradation of their properties (Juvandes, 2002; Odegard, 2011; Martins Dias da Silva, 2017). One of the determining factors for the excessively high market prices for stone composites is the commercial value of epoxy resins.

In *Calcinata* research project, binders produced based on carbonate sludge and polyester resins were studied, these resins being much more economical than epoxy resins and with good performance.

Figure 1: Deposit of carbonate sludge. Vila Viçosa, Evora, Portugal.

2. Materials and Methods

The methodology implemented respects a logical sequence in the investigation of carbonate sludge, considering their diversity, insofar as they come from the treatment of marble and sedimentary limestone. Thus, a sampling campaign was carried out in the Marbles Area (Estremoz, Borba and Vila Viçosa) and in the *Maciço Calcário Estremenho* area (Santarém) (Figure 2), followed by drying at room temperature and subsequent breakdown using a Retsch jaw mill – BB200.

The collection of marble carbonate sludge was carried out 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 carbonate sludge was collected at *Solancis - Sociedade Exploradora de Pedreiras SA*, referenced as C(S) and *MVC - Mármores de Alcobaça Lda*., referenced as C(MVC).

This was followed by a phase dedicated to the physical and chemical characterization of the carbonate sludge. 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. The particle size distribution of the fraction constituted by the e.s.d. > 0.63 mm, was determined by sieving, according to Standard E234 (LNEC E243, 1969). The particle size distribution analyses of the fraction smaller than 0.063 mm were carried out at the *Ambiterra* Laboratory, at the University of Évora, with the dimensional distribution of the particles being determined using a sedimentograph, Micromeritics, model Sedigraph 5100, with X-ray sources.

To determine the density of the carbonate sludge, which is essential for formulating the compositions, the EN 1097-7 standard - Determination of the filler density - Pycnometer method was used (EN 1097-7, 2022).

The chemical compositions carried out on the carbonate sludges were determined at the *Ambiterra* Laboratory, at the University of Évora, based on the fractions < 63 µm, determining the redness loss and the contents of the following major elements: Mn, Ti, Ca, K, Si, Al, Mg, Na and Fe, expressed as oxides: MnO, TiO_2, CaO, K_2O, SiO_2, Al_2O_3, MgO, Na_2O and Fe_2O_3, through Optical Emission Spectroscopy with inductive plasma source (ICP-OES). After the characterization phase, a new stage began with the constitution of formulations with different percentage contributions of carbonate sludge and polyester resin, branded Recapoli 2196 and subsequent physical-mechanical evaluation. The mixtures were carried out using a manual mixer, and were subsequently deposited in moulds with 15 cm x 15 cm x 15 cm. To evaluate the evolution of strength values over time, the formulations were initially tested with three curing times: 7 days, 14 days and 28 days. At the end of the established periods, the cubic blocks were cut into 5 cm x 5 cm x 5 cm specimens and subjected to uniaxial compression strength tests, in accordance with the EN 1926:2008 standard (EN 1926, 2006) and using a Pegasil compression press.

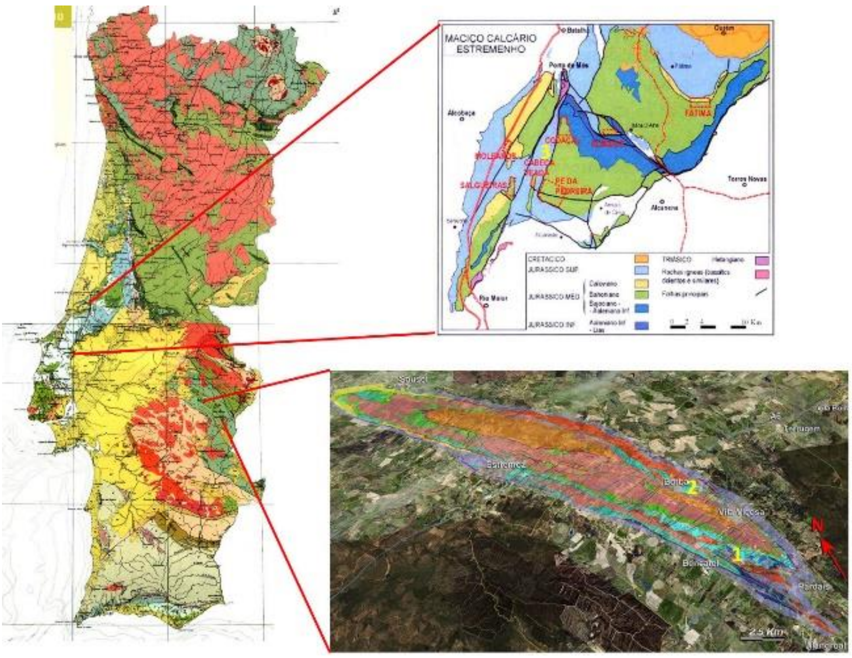

Figure 2: Sampling location on a geological basis. 1 – Carbonate sludge from *Texugo* quarry (*António Galego & Filhos*). 2 – Carbonate sludge from the JPL quarry (*Marmetal / A.L.A. Almeida*). 3 – Carbonate sludge from Cabeça Veada quarry (*Solancis* and *MVC*).

3. Results and Discussion

3.1. Particle Size distribution analysis

The particle size distribution analyses showed great similarity between the granulometric distributions of the constituent particles of the limestone samples among themselves, as it happens in the granulometric distributions of the constituent particles of the marble samples. This similarity is shown in Figure 3.

3.2. Density

Density was determined according to the NP EN 1097-7 2002 standard and 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 and C(MVC) – 2.493 g/cm^3.

3.3. Chemical Characterization of Collected Samples

Using the aforementioned methodology, results were obtained regarding the contents of the following major elements: Mn, Ti, Ca, K, Si, Al, Mg, Na and Fe, expressed in the form of oxides: MnO, TiO_2, CaO, K_2O, SiO_2, Al_2O_3, MgO, Na_2O and Fe_2O_3, listed in Table 1.

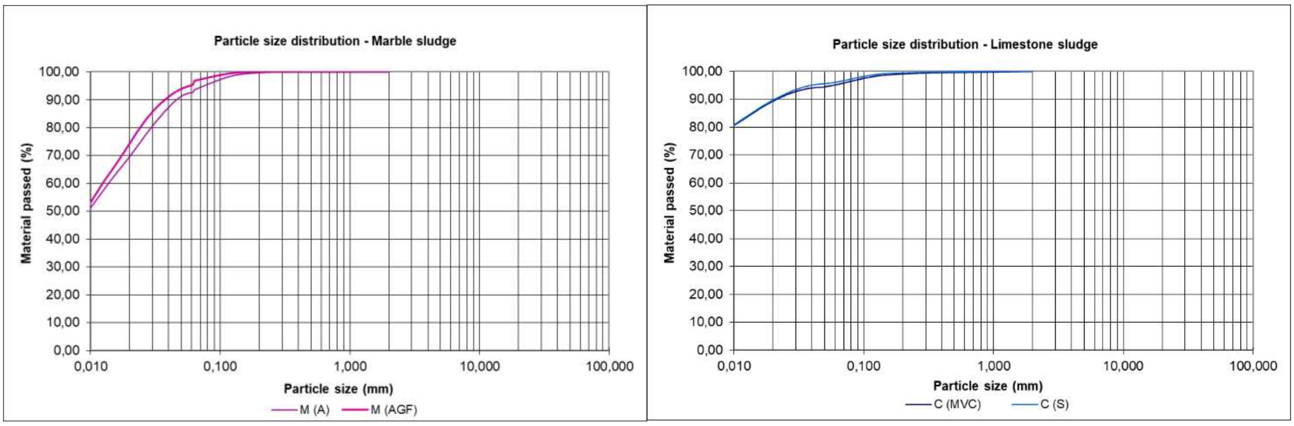

Figure 3: Particle size distribution of the testes samples: M(A), M(AGF), C(MVC) ad C(S).

Table 1: Percentage of major elements in the four carbonate sludge samples.

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

3.4. Mineralogical composition of carbonate sludge

The previously disaggregated samples were subjected to sieving, obtaining the fraction composed of particles with an equivalent spherical diameter of less than 63 µm. This fraction allowed for a global mineralogical analysis, represented in Figure 4.

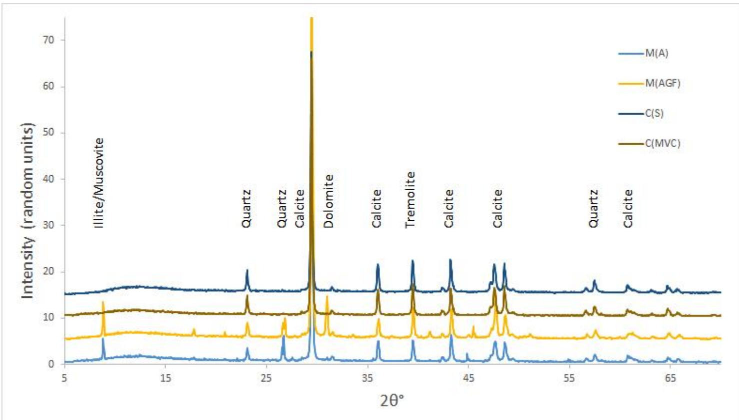

Figure 4: Diffractograms referring to the analysed marble and limestone samples.

3.5. Mechanical Characterization of Binders

The mechanical characterization of the binder is fundamental to validate its performance, since its mechanical behaviour will condition the mechanical behaviour of the composites that incorporate it. At this stage, it was important to evaluate the uniaxial compression strength of the different formulations with different percentage contributions of carbonate slurry and resin. Based on the results obtained, in conjunction with the results of the physical characterization of these formulations, it will then be possible to define the optimal composition of the binder. Thus, some preliminary formulations were carried out in a laboratory context, with a view to determining the compositions that would guarantee more homogeneous and more compact mixtures, starting then with moulded mixtures in moulds measuring 15 cm x 15 cm x 15 cm (Figure 5).

Figure 5: Moulds filled with the mixtures of binder with carbonate limestone and marble sludges and Recapoli resin.

After demoulding, 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. These results are shown in Table 2.

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

4. Conclusions

This work highlights the importance of characterization and research on carbonate sludges to allow the development of sustainable stone composite materials. This study included the analysis of four different carbonate sludge: two from limestone and two from marble processing.

Results allow to reach the following conclusions:

- Particle size Analysis – Despite being collected in various places, there is great granulometric proximity between the samples of calcareous nature and between the samples of marble nature.
- Mineralogical Composition - M(A), M(AGF), C(S) and C(MVC) – carbonate sludge markedly carbonate, with peaks in XRD, well defined in Calcite.
- Chemical Composition - All carbonate sludges with significant percentages of CaO and at loss of ignition test (C(MVC) – 43.50%; C(S) – 43.30%; M(AGF) – 42.97%; M(A) – 42.15%). M(AGF) and M(A) expressed in SiO2 and M(AGF) something magnesium (MgO).

It was found that the results obtained for the mixture composed of 50% limestone carbonate sludge and 50% resin exceeded by 4MPa the values obtained for the same formulation with marble carbonate sludge. On the other hand, formulations with 47% of carbonate sludge and 53% of resin allowed identical results for limestone and marble sludges. At a proportion of 52% carbonate sludge and 48% resin, the formulation with marble carbonate 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. In addition, to the use of carbonate sludge which also allow reducing the amount of resin used, guarantee consumption of a product hitherto treated as waste. The percentage reduction of resin as a binder, due to the incorporation of carbonate sludge, is favourable, as the amount of resin in the composites is reduced. This research clearly opens a field of investigation to the use of a residue from the natural stone extractive industry pointing to innovative solutions for carbonate sludges, commonly deposited in the open with obvious environmental impacts.

Research will continue with the formulation of different compositions integrating aggregates from marble crushing, with different granulometry, thus constituting more environmentally sustainable stone composites.

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