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Characterization of historical mortars from Santa Catarina (Brazil)

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ABSTRACT

The aim of this research is to characterize the mortars (binder and aggregate) of nine historical buildings, built between 1750 and 1922, in the State of Santa Catarina, Brazil, using X-ray diffraction (XRD), thermogravimetry (TG), Fourier transform infra-red spectrometry (FT-IR) and atomic absorption spectrometry (AAS). The compositions and granulometric distributions of the aggregates were determined by sedimentology, and the aggregate content was estimated by hot hydrochloric acid attack.

The results showed that the principal binder is hydrated lime, obtained from the burning of seashells, in some cases mixed with hydraulic materials (clay, ground ceramic tile or brick, and hydraulic lime). The results of the hot HCl attack revealed three average binder/aggregate ratios.

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1. Introduction

The rehabilitation of historical buildings is very important in terms of the history and culture of cities. Inadequate intervention in historical buildings and the use of Portland cement-based mortars to restore historic renderings can cause more damage than benefit through negative interactions between the cement and the original materials (bricks, stones or binders) [1]. The damage caused is due to the fact that, if compared to historical mortars, Portland cement-based mortars (i) are less permeable, retained an excess water which can generate alteration phenomena; (ii) have a high content of soluble salts triggering intense corrosion of the original materials through salt decay; (iii) are less able to accommodate the masonry structure movements (thermal and humidity effects, creep) due to its higher hardness and rigidity [2–5]. Therefore, firstly, a historic-scientific study of the original material needs to be carried out before any intervention in historical buildings, and, secondly, the data obtained must be used either to produce a similar material or to formulate a restoration mortar from modern materials without significant negative interactions with the pre-existing materials.

Historical mortars are complex systems, containing aerial or hydraulic binders or a blend of them, aggregates (not always crystalline) and admixtures that interact with the binder [6]. The use of techniques for microstructural characterization of materials, e.g. optical and electron microscopy, X-ray diffractometry, thermal analysis, infra-red spectroscopy, chemical analysis, etc., allows for the determination of the composition and of some characteristics of the mortars. However, each technique has its own limits and in many cases several characterization techniques must be used to obtain coherent and reliable results [7]. Such modern techniques of investigation have been used to characterize Roman and medieval mortars [3,4,8–13].

The characterization of the binder allows the classification of the mortars as typical lime mortars, crushed brick-lime mortars, rubble masonry mortars, cementitious mortars and mortars with gypsum [3,11]. However, these studies did not investigate the origin of the lime, which could be mussel shells, natural limestone or other sources.

The first binder used in Brazil was calcareous, obtained from the seashell deposits that coated the sea-bed in Baía de Todos os Santos (All Saints Bay) in the 16th century, in the city of Salvador [14]. Locals have reported that mixtures of 'seashell lime', sand and whale or fish oil were used for the production of mortars used in the construction of many historical buildings in Brazil. In Florianópolis, Santa Catarina State, Caieira beach was historically known as the place where quicklime was produced from seashells, extracted from extensive millenarian deposits, that were burnt in holes in the ground. However, this artisanal process discontinued with the beginning of industrial limestone mining (around 1940). Thus, it seems that the main historical mortars in Brazil were composed of sand, whale or fish oil, and lime obtained from the burning of oyster shells and/or coral blocks in artisanal kilns [15].

The main purpose of this research is to identify and characterize the binders and aggregates of mortars used in nine historical buildings built in Brazil between 1750 and 1922 in the cities of Florianópolis, Laguna and São Francisco do Sul, all of them in the State of Santa Catarina, southern Brazil. The final goal is the formulation of restoration mortars.

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2. Materials and methods

Nine rendering mortars extracted from historical constructions were studied. The function, age and provenance of the mortar samples are shown in Table 1.

The samples were removed from the rendering mortar of masonry walls at an approximate height of 130 cm from regions apparently not damaged. Three 150 g samples were extracted from each of the nine buildings with a chisel. Their external part was scraped off and discarded in order to ensure the collection of non-altered material [16].

For the characterization of the binder and of the aggregate, the sample was gently ground in a porcelain mortar. The fraction passing through a sieve number 200 (US Standard Sieve Openings – 0.074 mm) was considered as the binder [17].

Approximately 150 mg of the fine binder powder was used for the thermal analysis; for the other tests (500 mg for XRD, 10 mg for FT-IR, 5 g for AAS and 5 g for the gravimetric analysis) the powder was dried at a temperature not higher than 70 °C to avoid the elimination of organic compounds.

X-ray diffractometry (XRD) was performed with a Philips powder diffractometer to determine the nature of the crystalline components. The type and content of lime and the presence of hydraulic binders were determined by thermogravimetric analysis (TGA) (Netzsch STA 409EP). TGA has been used to classify mortars as typical lime mortars, crushed brick-lime mortars, rubble masonry mortars, cementitious mortars and mortars with gypsum [3,11]. The temperature in a nitrogen atmosphere was raised from ambient temperature to 1000 °C at a constant heating rate of 10 °C/min. Fourier transform infra-red (FT-IR) spectrometry was used to detect the presence of salts and organic compounds and to confirm the results obtained from the thermal analysis and the XRD. Atomic absorption spectrometry (AAS) was used to identify and quantify oxides, and gravimetric analysis was used to quantify the silica.

The aggregate obtained after the gentle grinding and sieving of the mortars was washed with water to eliminate possible salts, and dried at 70 °C. The sedimentological analysis provided information on the maximum, minimum and characteristic grain diameters, the grain size distribution, the probable origin of the aggregate (dune, river or sea sand), and the mineral composition, from 30 g samples.

The binder/aggregate ratio was determined by the dissolution of the mortar samples through hot hydrochloric acid attack, as described in [16].

3. Results and discussion

3.1. Binder identification and characterization

The XRD results (Table 2) indicated that calcite is the main component of the binder, and that quartz is present in the smaller aggregate grains which passed through the 74 μm sieve. In some samples the presence of clay minerals, such as kaolinite (basal interplanar distance d_{hkl} = 7.17, 1.49, 3.58 Å) and kaolinite-smectite – Al–Si–O–OH–H_2O (d_{hkl} = 7.24, 4.31, 3.55 Å), could be detected, as well as traces of anortite (d_{hkl} = 3.20, 3.18, 4.04 Å) and gehlenite (d_{hkl} = 2.86, 1.93, 1.82 Å), and a small amount of calcium silicate hydrate (d_{hkl} = 3.27, 2.42, 4.22 Å) which indicates the presence of hydraulic compounds.

Table 2
XRD binder characterization.

	Calcite	Quartz	Calcium silicium hydrate	Kaolinite–smectite	Kaolinite	Gehlenite	Anortite
LAG1	++++	++	++	++	+++	+	t
LAG2	++++	+	+	+	++	–	t
LAG3	++++	++	++	+	++	t	+
SFS1	++++	+	++	t	+	t	–
SFS2	++++	+	++	–	–	–	t
SFS3	++++	+	t	–	+	t	–
FLN1	++++	+	+	–	–	–	–
FLN2	++++	+	t	–	–	–	–
FLN3	++++	+	–	–	–	–	–

Peak intensity: ++++: very strong, +++: strong, ++: medium, +: weak, t: traces, –: not found.

Table 3 shows the results of the TG analysis. According to the classification proposed by Moropoulou et al. [6] and Bakolas et al. [11], the weight loss up to 120 °C is due to adsorbed water which is characteristic of the presence of hydraulic binders that are hygroscopic. The weight loss in the temperature range 120–200 °C is attributed to the crystallization water of hydrated salts that may originate from the sulfatation of carbonates, accumulation of salts in the masonry, or the presence of gypsum in the original binder. The weight loss between 200 and 600 °C is attributed to the loss of the chemically bound water of hydraulic compounds (C–S–A–H and/or C–S–H) when techniques such as XRD, FT-IR do not detect other compounds that decompose in the same temperature range, such as calcium hydroxide, magnesium hydroxide, hydromagnesite, organic compounds, etc. The weight loss above 600 °C is due to the decomposition of carbonates. Furthermore, the CO_2/H_2O ratio, i.e., the ratio of the weight loss due to the decomposition of carbonates (>600 °C, in%) to that attributed to the chemically bound water of hydraulic compounds (200–600 °C, in%), can provide important information regarding the hydraulic nature of the binder [4,6,11,18]. It is well known that as the hydraulic character of the binder increases, the weight loss between 200 and 600 °C increases, the weight loss above 600 °C decreases, and the CO_2/H_2O ratio decreases [3,4,11,18–20]. In Fig. 1, three distinctive groups of binder were identified, whose characteristics are showed in Table 4 [18], leading to the following classification of the mortars:

Table 1
Mortar description.

Mortar	Function	Date of construction	Provenance[a]
FLN1	External rendering mortar	Nearly 1750	Vicar's house of the Lagoa da Conceição Church – Florianópolis
FLN2	Internal rendering mortar	Nearly 1750	Nossa Senhora das Necessidades Church of Santo Antônio de Lisboa – Florianópolis
FLN3	Internal rendering mortar	1806	Nossa Senhora da Lapa do Ribeirão Church – Florianópolis
LAG1	Internal rendering mortar	1850–1900	Mansion – Laguna
LAG2	Internal rendering mortar	1800–1850	Mansion – Laguna
LAG3	External rendering mortar	Around 1800	Historical hotel – Laguna
SFS1	Internal rendering mortar	Around 1900	Mansion – São Francisco do Sul
SFS2	External rendering mortar	1922	Mansion – São Francisco do Sul
SFS3	External rendering mortar	Around 1900	Terminal Marítimo – São Francisco do Sul

[a] The environmental conditions are the same for all mortars (coastal and sub-tropical) with an average RH and temperature around 80% and 21 °C, respectively, over the year.

Table 3
TGA results for the binder according to the classification proposed by Bakolas, Moropoulou, and co-workers [6,11].

	$T < 120$ °C[a]	120–200 °C[a]	200–600 °C[a]	$T > 600$°C[a]	CO_2/H_2O
LAG1	1.53	0.23	7.04	19.34	2.75
LAG2	1.39	0.74	8.26	18.9	2.29
LAG3	1.12	0.00	8.30	12.03	1.45
SFS1	1.14	0.31	5.19	25.88	4.98
SFS2	1.42	1.42	5.35	20.35	3.80
SFS3	1.15	0.83	4.47	30.34	6.78
FLN1	1.26	0.68	4.29	31.86	7.43
FLN2	1.09	0.61	4.44	34.93	7.87
FLN3	0.62	0.60	3.85	39.39	10.23

[a] % Weight loss.

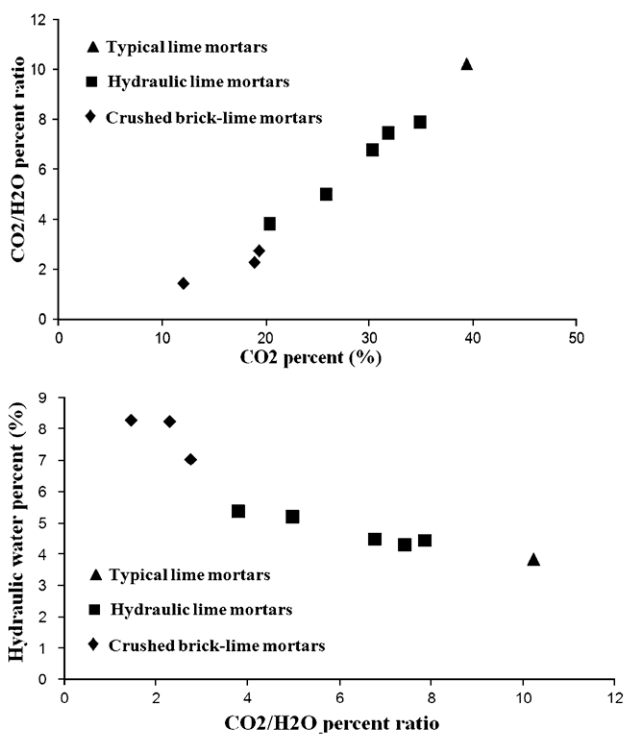

Fig. 1. (a) Percent CO_2/H_2O ratio vs. CO_2. (b) Percent hydraulic water vs. CO_2/H_2O ratio.

(a) Typical lime mortars (FLN3) with hydraulic water <4% and $CO_2/H_2O > 10$.
(b) Hydraulic lime mortars (FLN1, FLN2, SFS1, SFS2 and SFS3) with intermediate hydraulic character with hydraulic water between 4% and 6% and CO_2/H_2O between 4 and 9.
(c) Crushed brick-lime mortars (LAG1, LAG2 and LAG3) with higher hydraulic character than the hydraulic lime mortars with hydraulic water between 6% and 10% and $CO_2/H_2O < 4$.

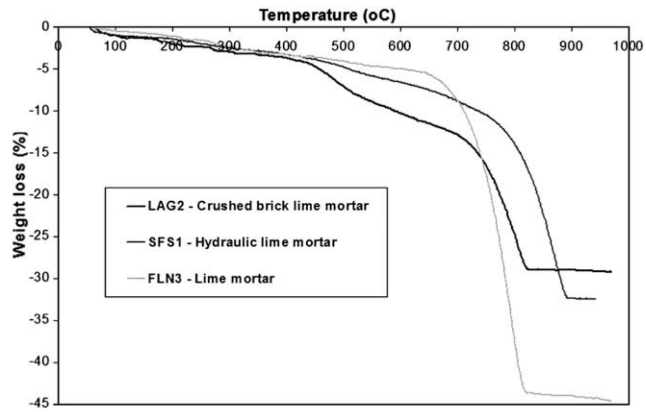

Fig. 2. Typical TGA curves of the three groups of mortar binders: lime, hydraulic lime and crushed brick-lime.

Fig. 2 shows typical TGA curves of the three groups of binders. The binder in lime mortars is a typical hydrated or air-lime mortar which has become totally carbonated over time. The slightly hydraulic character of the binding material in hydraulic lime mortars is attributed to the presence of impurities (silica) in the raw carbonate material or to the accidental introduction of 'clayed materials' during the lime production, since it is known that historically ovens were covered with clay before burning. The highly hydraulic character of the binder of crushed brick-lime mortars is due to the use of marly lime, as mentioned above, and also to lime/ceramic dust interactions [4,11,18]. The mixture of burnt clayed material (e.g. crushed brick) to lime was used in ancient times by the Phoenicians (10th century BC) as a way to improve the bearing capacity and durability in a marine atmosphere [1,20,21]. The hydraulicity results from interactions between the calcium hydroxide and silicates, silico-aluminates and aluminate present in the crushed ceramic material which is not well burnt, leading to the formation of cementitious compounds such as C–S–H, C–S–A–H and C–A–H [1,3,4,11,22–24].

The infra-red analysis (FT-IR) confirmed the TGA and XRD results, as follows:

(i) All binding materials show the absorption bands of carbonates (2870, 2515, 1798, 1427, 876, 709 cm^{-1}) [25–27]: the stronger the hydraulic character of the binder the less intense the bands.
(ii) Mortars with hydraulic binders show absorption bands due to silicates and alumino-silicates (1110, 1033, 790, 756, and 539 cm^{-1}) [25] which are more intense for more hydraulic binders.
(iii) Organic compounds and hydrate salts were not detected.

Atomic absorption spectrometry – AAS allows the quantification of the oxides in the binder, as well as the estimation of the binder hydraulicity through the cementation index – CI [Eq. (1)]. The higher the CI, the more hydraulic the binder [2]. As expected, the AAS results (Table 5) showed that as the hydraulic character of the binder increases the CI index increases.

Table 4
Binder classification (adapted from [18]).

Mortar type	$T < 120$ °C (hygroscopic water)	200–600 °C – H_2O (hydraulic water)	$T > 600$ °C – CO_2 (decomposition of carbonates)	CO_2/H_2O	Sample
Lime mortars	<1	<4	>30	>10	FLN3
Hydraulic lime mortars	>1	4–6	20–34	4–9	FLN1, FLN2, SFS1, SFS2*, SFS3
Crushed brick-lime mortars	>1	6–10	12–20	<4	LAG1, LAG2, LAG3

* SFS2 shows characteristics of both hydraulic lime and crushed brick-lime mortars.

Table 5
Chemical analysis of the binder (%wt) and cementation index – CI.

	CaO (%)	SiO_2 (%)[a]	Al_2O_3 (%)	Fe_2O_3 (%)	MgO (%)	CI[b]
LAG1	12.46	29.63	5.81	2.60	0.18	7.17
LAG2	18.23	30.56	5.87	1.19	0.11	5.05
LAG3	15.01	29.37	5.78	2.62	0.21	5.90
SFS1	29.81	19.42	2.76	1.36	0.21	1.93
SFS2	23.00	25.76	2.13	1.07	0.64	3.15
SFS3	34.59	19.00	1.41	0.44	0.17	1.58
FLN1	40.64	7.84	0.76	0.61	0.55	0.56
FLN2	47.07	3.85	1.84	0.29	0.11	0.28
FLN3	48.69	1.92	0.41	0.21	0.41	0.12

[a] Quantified by gravimetric analysis.
[b] CI < 0.3 – aerial; CI = 0.3–0.5 – low hydraulicity; CI = 0.5–0.7 – moderate hydraulicity; CI = 0.7 to 1.1 – hydraulic.

$$CI = \frac{2,8x\%SiO_2 + 1,1x\%Al_2O_3 + 0,7x\%Fe_2O_3}{(\%CaO + 1,4\%MgO)} \tag{1}$$

The AAS results also show that the lime used in all mortars is calcitic, with magnesium only present in trace amounts (0.11–0.64%). However, the lime produced in the coastal region of Santa Catarina is dolomitic (CaO/MgO between 1.2 and 1.4), leading to the following hypotheses about the origin of the lime used in the mortars:

1. The lime, produced with calcitic limestone as the raw material, was "imported" from other Brazilian states such as Minas Gerais.
2. The lime was manufactured from the burning of mussel shells.

The first hypothesis is reasonable, but its probability is very low due to the lack of transport facilities in historical times which led to high transportation cost and to a preference for local materials. The use of 'seashell lime' is thus the most realistic hypothesis, although no information on its use in historical mortars could be found in the literature, probably because of the local aspect of this type of production.

3.2. Aggregate identification and characterization

The sedimentological analysis showed that the aggregates were composed mainly of quartz, feldspar, some traces of mica, rock residues and seashell fragments. The analysis allowed the classification of the aggregates into two groups: beach sand for the São Francisco do Sul mortars (SFS1, SFS2, SFS3), and river sand for the others (LAG1, LAG2, LAG3, FLN1, FLN2, FLN3).

The grain size distributions of the sands are continuous. The maximum and minimum dimensions of the sand grains are 2.8284–0.0884 mm for three of the buildings (FLN2, SFS1 and LAG2) and 2.8284–0.0625 mm for the others.

Silts and clays were not detected. The percentage of seashells in the aggregates varies from 7.73% in the LAG2 mortar to 46.03% for FLN1 mortar. The gravel percentages in the sands are highest for FLN2 19.52%, LAG2 – 16.73%, LAG2 – 14.95%, SFS3 – 10.33% and SFS2 – 7.67%; and for the other mortars these percentages are low. The method of hot HCl attack [16] allowed the classification of the mortars according to their binder/aggregate ratio into three groups: 1:1.2 (FLN1, FLN2); 1:2 (FLN3, LAG1, LAG2, LAG3, SFS2, SFS3); and 1:3.44 (SFS1).

It is worth noting that the proportion of aggregates decreases with the age of the building. The higher aggregate amount may have been used in an attempt to prevent cracking or due to economic aspects.

3.3. General considerations

Via visual inspection, it was found that the majority of the rendering mortars analyzed in this research are in an excellent state of conservation, despite their advanced age (more than 100 years-old), considering that some of them are in a state of total abandonment. This durability is essentially due to the fact that lime-based mortars do not release soluble salts and are more chemically, structurally and mechanically compatible with the ancient masonry [2,4,6,11,27,28]. So, our recommendation is the use of similar original materials for the mortars restoration purposes of the studied buildings, for example seashell lime and clay brick dust as binder. However, the main problem is that these original ingredients are no longer available:

(a) "Modern" clay brick dust does not present the same physical and chemical characteristics as the traditional ones because production processes have changed a lot through the last century. For example, nowadays, the temperatures for clay brick production are higher than 900 °C and, to develop some pozzolanic activity, clay brick dust must be fired between 600 and 900 °C [21,29]).
(b) In the State of Santa Catarina, as mentioned above, commercial lime is originated from limestone mining which turns seashell lime production economically unviable.

However, two factors can lead to a regain of interest of the use of seashell lime for restoration purpose. The first one is that commercial lime originated from limestone mining produced in the coastal region of Santa Catarina State is dolomitic, and it is well known that, when compared to high calcium limes which is the case of seashell lime, the late hydration of MgO from dolomitic limes can be result in pitting [5] and the attack by SO_2 from polluted environments lead to the formation of deleterious magnesium sulfate salts [30]. The second one is due to a recent specificity of our region. Currently the coastal region of the State of Santa Catarina is leading the national production of oysters. However, such industry has a potential of serious problem about disposal of oyster shell waste which is, for the most part, illegally dumped into the sea, leading to serious environmental problems as, for example, waterfront silting.

Therefore, for restoration purposes and to ensure a compatibility with the old masonry, it can be considered the study of a repair mortar with a binder composed by high calcium lime from the burning of the oyster shell waste with small amounts of carefully controlled calcined clay dust. A binder:aggregate ratio between 1:2 and 1:3 was determined as a benchmark. However, further investigations on these materials are needed.

4. Conclusions

The main purpose of this study was to identify and characterize the binders and aggregates of mortars used in nine historical buildings in order to collect data that will be considered for the formulation of restoration mortars compatible with ancient masonry.

Seashell fragments were found in all of the mortars studied. From the XRD, TGA, AAS and FT-IR results it was possible to conclude that the main binder of the mortars is a calcitic lime manufactured from seashells, which was totally carbonated.

Regarding the binder composition, it was possible to classify the mortars into three groups:

1. Typical hydrated lime mortars in which the predominant binder is hydrated lime.

2. Hydraulic lime mortars with low hydraulic binder content, or marly lime mortars; the trace amounts of hydraulic compounds is probably due to impurities present in the raw material or they could have been introduced during the lime production.
3. Crushed brick-lime mortars with medium hydraulic binder content: lime mixed with small fragments or dust of ceramic materials.

The aggregates are of beach origin in the case of the San Francisco do Sul mortars (SFS1, SFS2 and SFS3), and the others are from river origin. They are mainly comprised of quartz and seashell fragments. Three average binder/aggregate ratios were measured: 1:1.2; 1:2; 1:3.44. It was also observed that the binder proportion is lower for the more recent buildings.

Thus, for restoration purposes, it was suggested the study of repair mortars with a binder composed by a mixture of seashell lime and calcined clay dust and, a binder:aggregate ratio between 1:2 and 1:3.

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