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Statistical analysis of the physical properties and durability of water-repellent mortars made with limestone cement, natural hydraulic lime and pozzolana-lime

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HIGHLIGHTS

- Water-repellent mortars prepared using siloxanes and metal soap admixtures.
- Chemical–physical properties assessed before/after exposure to salt solution.
- Data analysed by principal component analysis and linear regression models.
- The relationship between the properties in different environments is evaluated by statistical methods.

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ABSTRACT

Multivariate statistical methods are proposed for the analysis of the physical properties of limestone cement, natural hydraulic lime and pozzolana-lime mortars admixed with water-repellents. The relationship between the physical properties and the durability of the mortars is evaluated by principal component analysis (PCA) and linear regression models. PCA allows to visualize (i) three groups of mortars according to the binder used and the structural/mechanical properties; (ii) the durability in relation to the mortar properties in simulated conditions. Linear regression models allow to identify and quantify associations between properties, composition and durability.

1. Introduction

Water represents one of the most important degradation factors for porous building materials such as mortars, stones, bricks and concretes. The damages caused by water require high maintenance costs for the reparation of materials and structures not well protected [1–5]. Thereafter, a great extent of research has been developed for the formulation of water-repellent systems for reducing and minimizing the degradation processes [6–9]. Among the different systems developed, the most promising is the use of suitable water-repellent admixtures to prepare water-repellent mortars [10–16]. Accordingly, different hydrophobic compounds have been used as admixtures, for examples metal soaps such as calcium, zinc, sodium oleates or stearates and products based on silane/siloxanes [17–19]. Several of these commercial water-repellent admixtures are regularly used in Portland cement mortars, however their behaviour needs to be further investigated in mortars made with different binders, such as natural hydraulic limes mortars, artificial hydraulic limes mortars made with pozzolana, or blended cement mortars (e.g., limestone cement mortars). In comparison to Portland cement mortars, these mortars demonstrate physicochemical characteristics more compatible with different traditional building materials [20–23] and allow to reduce both the employ of energy and CO_2 emissions during production and use [24]. On the other hand, they had often lower durability in respect to the damaging action of water. However, higher durability could be assured by the use of water-repellents admixtures.

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In order to evaluate the suitability of water-repellent mortars as protective layers against the damaging action of water, it is necessary to adopt an integrated approach including a *first phase* aimed at studying the characteristics of the hardened mortars through different experimental techniques and the collection of substantial experimental data [10], followed by a *second phase* aimed at evaluating the consequences and damages due to the exposure to different types of decay [12]. In this sense, the evaluation of the exposure to salt weathering is of particular interest, since salt transport and crystallization inside porous building materials cause serious damages on many kinds of natural or artificial stone material and take place in a variety of environments [25].

In the last ten years some authors have proposed the use of multivariate statistical approaches in order to analyze the experimental data and simplify their interpretation [26–31]. In particular, statistical methods such as Cluster Analysis and Principal Component Analysis (PCA) have been successfully applied in chemometrics studies to reduce the data dimension, allow an intuitive visualization of the correlation between properties and classify or group different kind of objects/materials, archaeological findings, ceramics and mortars on the basis of their properties [28–34]. Despite this, PCA is not commonly used to study the mortars degradation [30].

PCA can be complemented with statistical modelling in order to quantify the association between different properties and parameters and to identify the factors that mostly influence the variation of parameters that serve as proxy for the environmental situation [35–38]. In fact, the modellization of the composition and/or different properties by linear regression models is an increasingly frequent approach to study the relationship between single properties and mortar composition. In most cases mortars with slightly different compositions (e.g. same binder type and different percentages of admixtures) are considered to verify the effects of specific admixtures on particular properties or to predict the behaviour of a specific composition [36–38]. Also the effect of different exposure conditions have been considered with good results [37].

This paper proposes a methodological approach based on multivariate statistical techniques such as PCA and linear regression models to study both the properties of water repellent mortars and the effects of the exposure to salt solutions.

The statistical methods were used in the attempt to: (i) classify the water repellent mortar samples in approximately distinct groups, depending on the physical and structural characteristics of the samples; (ii) highlight the different behaviour due to the weathering processes, in particular of samples exposed to the action of a damaging sodium sulphate solution; (iii) evaluate how different physical characteristics, such as the mortar composition, the strength, the porosity and the water absorption can influence the resistance to salt crystallization.

The data employed in the statistical elaborations were collected on hydraulic mortars with water-repellent properties, suitable for the restoration of historical buildings. Natural hydraulic lime, pozzolana-lime and limestone cement were used as binders, while water-repellent admixtures were selected among those most commonly used, namely, calcium and zinc stearate, powder silane/siloxane and silane water-based emulsions. Some of the water-repellent mortars, after one year of hardening, were exposed to the damaging action of a sodium sulphates solution (as suggested by the EN 12370 [39]), in order to evaluate the resistance to salt crystallization. Physical and structural properties such as density, porosity, mechanical strength, water-repellence properties, water vapor permeability were determined before and after the exposure together with the mass variations during the exposure.

Distinct PCAs were performed on the data collected before and after the exposure in order to highlight possible relationships between the properties and the decay due to the soluble salts. Furthermore, linear regression models were developed in order to link the properties measured on mortars before the exposure to the effects due to the exposure. To this aim, the percentage mass variation after the exposure was used as an indicator of degradation and modelled in terms of a list of appropriate predictors.

2. Experimental

2.1. Mortar preparation

Three distinct binders and eight different water-repellent admixtures were used to prepare 47 mortar mixtures (Table 1). The binders used were: a limestone cement (CEMIIB/L 32.5R), with a limestone content around 23% by mass (by CementiRossi®, Pederobba, Italy); a natural hydraulic lime (NHL 3.5) "Calce dei Berici" conform to EN 459-1: 2002 [40] (by Villaga SpA® Ceraino di Dolcé, Italy); a mixture of industrial lime hydrate (by BASF®) and the S&Bμ-silica®, a pozzolana of volcanic origin from Greece.

For each set, the following water-repellent admixtures were used: the modified silane/siloxanes in powder form Sitren P750, Sitren P730 (by Evonik®) and Silres A (by Wacker Chemie®); the water-based silane microemulsion Tegosivin HE 328 (by Evonik®); Calcium Stearate 82% (by Sigma Aldrich®); Zinc Stearate Pure (by Sigma Aldrich®); Vinnapas® 8031 H, a redispersible powder based on a terpolymer of ethylene, vinyl laurate and vinylchloride (by Wacker Chemie®); Socal U1S1 (by Solvay®), ultrafine calcium carbonate nanoparticles (Ø 40–130 nm) coated by calcium stearate. The concentration of water-repellent admixture used was of 1% by dry weight for each mortar set. Concentrations of 0.5% and 1.5% by dry weight were also tested in limestone cement mortars and some pozzolana lime mortars; only concentrations of 0.5% and 1% were tested for natural hydraulic lime mortars, since higher dosage led to incomplete hardening and curing of the specimens (we refer to [10,41] for a deeper insight on the influence of the water repellent on mortars hardening and curing). The specimens composition and the description of the water-repellent admixtures is listed in Table 1, while Table 2 displays the names of all the specimens included in the experimentation.

Sample preparation (mixing, demoulding and curing) was done according to the European standard EN 196-1 [42]. The water–binder ratio was adjusted in order to obtain a mortar slump of 170 ± 10 mm measured by flow table test, according to the method EN 1015–3 [43]. The specimens were prepared mixing the dry components following the proportion listed in Table 1 as dry powder in a planetary mixer at low speed (145 ± 10) rpm, then, water was poured on the dry components and the obtained mixture was worked for 3 min 285 ± 10 rpm. The water-based silane microemulsion Tegosivin HE 328® was diluted directly in the mixture water. The obtained mixtures were poured in polystyrene moulds for obtaining prisms $(4 \times 4 \times 16)$ cm^3 and demoulded after 2 days, then stored at RH = 90% and $T = (20 \pm 2)$ °C for 28 days. Some of the specimens were cut in order to obtain cubes $(4 \times 4 \times 4)\,cm^3$ or slices $(2 \times 4 \times 4)\,cm^3$. Mortars characterization was carried out as described in Section 2.3.

2.2. Determination of resistance to sodium sulphate crystallization

The resistance to salt crystallization of the water-repellent mortars was evaluated by immersion-drying cycles in a solution of sodium sulphate [39]. The method, based on the normative EN 12370 [39], was chosen in order to consider the serious damaging effect of sodium sulphates, and it is particularly effective in highlighting the resistance of mortars to salt crystallization [10]. Cubic mortar specimens added at 1% by dry mass were aged for one year at 23 °C and 65% RH before performing the cycles in order to have a completely hardened structure. At each cycle, the cubic specimens were immersed in a saturated solution of sodium sulphate decahydrate for two hours, followed by drying at 40 °C for 22 h in oven. The cycles continued till the disintegration of the specimens. Five cycles were possible on pozzolana-lime mortars, six cycles on natural hydraulic lime mortars and ten cycles on Portland limestone cement mortars. After each cycle, the specimens were dried in oven at 40 °C till constant mass and brushed with a soft brush to eliminate external incoherent salt efflorescences. The mass losses of the mortars were measured and the percentage mass variation ΔM was calculated as $\Delta M = (M_i - M_s)/M_s \times 100$, with M_s = starting mass and M_i = mass for the ith cycle. Positive mass variations are due to mass gain, negative mass variations are due to material loss. Mortars characterization was carried out after the cycles as described in Section 2.3.

In order to assure the comparison of the effects on specimens subjected to the same stress/testing conditions, the ΔM4th, determined after 4 cycles, was chosen as "degradation index" for all the mortar types. The fourth cycle was chosen because serious disaggregation of some specimens was observed for additional cycles of exposure (see also Section 2.5).

2.3. Mortars characterization

Different analytical techniques and test were performed in order to assess the physical and mechanical properties of specimens before and after the salt resistance test. For all the tests, the average of the results of three specimens for each mixture was considered.