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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Abstract

Multivariate statistics 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 proposed approach includes the evaluation by principal component analysis PCA and linear mixed models of the relationship between the physical properties and the durability of the mortars. PCA allowed to visualize i) three groups of mortars according to the binder used and to the structural/mechanical properties; ii) the effects due to exposure in relation to the mortar properties. Linear mixed effects models allowed to identify and quantify the association between the properties and the durability.

Keywords: Water repellent mortars, principal component analysis, linear mixed effects models, salt resistance, siloxane, metal soap, statistics methods.

1.Introduction

Water represents one of the most important degradation factors for porous building materials such as mortars, stones, bricks, 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 chemical-physical 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], but 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.

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 to study the characteristics of the hardened mortars and a second phase to evaluate the consequences and damages due to the exposure to different types of decay [12]. The evaluation of the exposure to salt weathering is of particular interest, since salt transport and crystallization inside porous building materials is a process that takes place in a variety of environments and affects many kinds of natural or artificial stone material, causing serious damages [25].

The study of the physical-chemical and structural characteristics of mortars can be done considering different experimental techniques and obtaining several experimental data [10]. The dimension of the data and the relationships between the data components often complicate the development of models to evaluate specific environmental conditions. In the last 10 years some authors have proposed the use of multivariate statistics approaches in order to compare the data obtained from the various analytical techniques used for characterising mortars and simplify their interpretation [26-30]. In particular, statistical methods analysis such as Cluster Analysis and Principal Component Analysis (PCA) have been successfully used to classify or group different kind of mortars comparing their physical and chemical properties. The PCA is an attracting statistical tool to reduce the initial number of variables (i.e. the measured properties) minimizing the loss of information, therefore, allowing an intuitive visualization of the correlation between the different properties/data [31-33]. Statistical modelling methods can be employed to quantify the association between different properties and parameters and to identify which factors mostly influence the variation of parameters, proxi of the environmental situation or the effects due to a specific weathering exposure [34].

This paper proposes a methodological approach based on multivariate statistical techniques such as PCA and linear mixed effects models **[35]** 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 more or less distinct groups, depending on their physical and structural characteristics; ii) highlight the different behaviour due to the weathering processes, in particular of samples exposed to the action of damaging salt solutions; iii) evaluate how different physical characteristics, such as the mortar composition, their strength, porosity, water absorption ,can influence the durability and in particular the resistance to salt crystallization.

The data for 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 between 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 sodium sulphates solutions (as suggested by the EN 12370 [36]), in order to evaluate their 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 or after the exposure in order to highlight possible relationships between the properties and the decay due to the salts. Furthermore, linear mixed effects models were developed in order to link the properties measured on mortars before the exposure to sodium sulphate solutions and the capillary absorption or the effects due to the exposure. To this aim, the percentage mass variation after the exposure was used as a indicator of degradation and modelled in terms of a list of appropriate predictors.

2.Experimental

2.1 Mortar preparation

Three different 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 [37] (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.

Eliminato: mortar

Commentato [UNIVE1]: The NHL was produced and bought in 2010 before the EN 459-1:2010 came into force, and used in 2011 for the preparation of the specimens.

For each set, the following water-repellent admixtures were used in concentration of 0.5%, 1% and 1.5% by dry weight: the modified silane/siloxanes in powder form Sitren P750, Sitren P730 from Evonik® and Silres A from Wacker Chemie®; the water-based silane microemulsion Tegosivin HE 328 from Evonik®; Calcium Stearate 82% (Sigma Aldrich®); Zinc Stearate Pure (Sigma Aldrich®); Vinnapas® 8031 H, a redispersible powder based on a terpolymer of ethylene, vinyl laurate and vinylchloride; Socal U1S1-Solvay®, ultrafine calcium carbonate nanoparticles (Ø 40-130 nm) coated by calcium stearate. The complete list of the specimens and their composition is listed in Table 1.

Sample preparation (mixing, demoulding and curing) was done according to the European standard EN 196-1 [38]. 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 minutes (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 (4x4x16) cm^3, demoulded after 2 days, and stored at RH= 90% and T= (20±2) °C for 28 days. Some of the specimens were cut in order to obtain cubes (4X4X4) cm^3 or slices (2X4X4) cm^3. Mortars characterization was carried out as described in paragraph 2.3.

2.2 Determination of resistance to salt crystallization

The resistance to salt crystallization of the water-repellent mortars was evaluated by immersion-drying cycles in a solution of sodium sulphate [36]. Cubic mortar specimens added at 1% by dry mass were aged for one year at 23°C and 65% RH before performing the test 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 hours in oven. The test continued till the disintegration of the samples. Four cycles were done on pozzolana-lime mortars, 6 cycles on natural hydraulic lime mortars and 10 cycles on Portland limestone cement mortars. The mass losses of the mortars were measured after each cycle and the characterization was carried out before and after the cycles as described in paragraph 2.3. The ΔM of the 4th cycle was chosen in order to compare the effects for mortars with different binders, before the complete disaggregation of some of the specimens.

Eliminato: s

2.3 Mortars characterization

Different analytical techniques and test were done 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.

Eliminato: structural

The structure was evaluated through measruments of : bulk density BD of hardened mortar prisms; real density RD (measured on grinded samples with a Micromeritics 1305 multivolume helium pycnometer); total cumulative volume of mercury intruded (TCV) linked to the total open porosity with a ThermoQuest/Finningam Pascal 140 and Pascal 240 mercury porosimeter MIP [39; 40]. In order to provide further information regarding the structure with a non-destructive evaluation, ultrasonic measurements US were done on prismatic specimens with a Controls 58-E4800 UPV with standard piezoelectric sensor at 45 Hz (cylinder 5cm Ø X5cm h), pulse rate 2 s, resolution 0.1μs. A direct configuration of the measurements, e.g. transmitter and receiver at the opposite sides of the specimens, was done along the longitudinal and transverse axes [41].

Eliminato: and bulk density (BD MIP) both

The compressive strength CS was measured with a Zwick/Roell Z010 press (pre-load 20 N, loading rate 50N/s) on prismatic samples according to UNI EN 12390-5:2009 [42].

Properties related to the behaviour in respect to water and water vapour such as water vapour permeability (P) [43,44], capillary water absorption coefficient C [45], surface wettability a (determination of contact angle according to NorMAL 33/89 with a Data Phisic ETT/XL instrument [46]) were measured too. The ionic conductivity of the samples was measured to evaluate the total soluble salt content as described by Normal 13/83 [47] on samples collected from the specimens at a 0.5-1 cm depth.

2.4 Principal component analysis

Among the multivariate statistical methods, PCA was chosen in order to achieve a reduction of dimensionality, thus allowing an easier visualization of the relationships between the parameters. The interpretation of the analysis allows also to evaluate the presence of mortars with similar behavior. The statistical software R [48] was used to elaborate the data. Given the different scales of measurement, PCA has been performed on the correlation matrix.

A first PCA was performed on the data collected on 28 day’s hardened mortars. The physical parameter used as variables for this PCA were: i) physical and structural properties of the hardened mortars, i.e the real density RD, the bulk density BD, the total cumulative volume TCV, the ultrasonic measurements US, the compressive strength CS; ii) properties regarding the behaviour of the hardened mortars in respect to water, i.e. the capillary water absorption C; the water vapour permeability P and the wettability *a* (contact angle).

Two separate PCAs were also performed on the data showed in Table 1 in order to evaluate the durability of the mortars and , in particular ,to visualize the situation before and after the test of resistance to salt crystallization,. The variables considered for the two analyses were: the total cumulative volume TCV, the compressive strength CS, the capillary water absorption C, the ionic conductivity "*cond"* of the samples on the outer part (0.0-0.5 cm depth), the ratio between the specimens mass before or after the test and the starting apparent volume (M/V_i). This ratio correspond to the bulk density only for the specimens before the exposure. Since during the test the damages due to the exposure caused huge material losses, then M/V_i could be considered a "damage parameter" providing a measure of the material loss due to the test. Lower values of M/V_i indicate higher mass loss and lower resistance to the physical decay.

2.5 Linear mixed effects models

We considered linear mixed effects models [35] to study the variables associated to variations of i) the capillary water absorption coefficient C and ii) the resistance to the action of sodium sulphate described by the measure ΔM (percentage mass variation after four cycles) chosen as a "degradation parameter".

Linear mixed effects models assume that the expected value of the response variable, namely C or ΔM, can be approximatively described as a linear combination of a set of esplicative or predictive variables. In order to account for the heterogeneity between the samples, a random intercept is included in the model. Denote by Y_{ij} the response variable for sample i (i = 1,...,20) and specimen j (j = 1,2,3), and let $x_{1,ij},...,x_{p,ij}$ be p explicative variables. Then, the linear mixed model with random intercept is:

$$Y_{ij} = \beta_0 + \beta_1 x_{1,ij} + ... + \beta_p x_{p,ij} + \mu_i + \varepsilon_{ij},$$

where β_0 is the model intercept, $\beta_1, \ldots, \beta_p$ are the coefficients measuring the contribution of the explicative variables, μ_i is the random intercept that accounts for the departures from the expected value due to the specific sample i and ε_{ij} is an error term. Model parameters are estimated under traditional distributional assumptions, namely random intercepts μ_i assumed to be realizations of independent normal variables with zero mean and variance σ^2, and errors ε_{ij} assumed to be realizations of independent normal variables with zero mean and variance τ^2. Furthermore, random intercepts are assumed to be mutually independent of error terms.

The capillary water absorption C should be linked to the admixtures effectiveness and should influence also the durability in different environmental conditions, therefore we consider the study of the variables associated to C is of particular interest in order to evaluate the durability of the mortars.

The mass variation ΔM is another simple parameter that can be used in order to evaluate the effects of the exposure: positive mass variation can be linked to the formation of salts inside the mortar structure, negative mass variation can be linked to material decohesion and losses due to specimens degradation.

Linear mixed effects models were developed on the available data consisting in 20 samples, type CM, NM or PM with the admixtures Silres A, Sitren P750, Sitren P730, Tegosivin HE 328, Calcium stearates, zinc stearates at 1% by mass, formed by three specimens each. The model used to identify variables associated to C include as potential explicative variables the compressive strength CS, the total cumulative volume TCV, the real density RD, and factors linked to the mortar composition (binder type PM pozzolana-lime, CM limestone cement, NM natural hydraulic lime mortars) and admixtures (siloxanes, stearates or none). Models for ΔM employ the same potential explicative variables with the addition of C.

Models are fitted with the maximum likelihood method as implemented in the R package nlme [49]. Model selection is based on a stepwise procedure using the Akaike Information Criterion (AIC). Validity of model assumptions is assessed through graphical inspection of residuals.

3. Results and discussion

3.1 PCA analysis of hardened mortars

The data related to the hardened mortars are listed in Table 2. The interpretation of the PCA results is based on bi-plots, which provide a convenient overview of the correlation between the different variables and their relationship with the objects/samples. In our application, bi-plots involving the first three principal components are sufficient since these components capture the 86% of the variance (Table 3).

The Bi-plots in Figure 1 and 2 and the coefficients of the components listed in Table 3 allow to recognize the role of the different variables in the samples differentiation. In particular the bulk density shows high positive loading on the first PCA component (PCA1), while the total cumulative volume and the water vapour permeability show negative loadings (therefore, negatively correlated to the bulk density). PCA1 seems to group the variables linked to the structure/microstructure of the sample. Interestingly the water vapour permeability has also an important weight on this component and it is correlated with the porosity values (both BD and TCV). The mechanical strength and the ultrasonic measurements are positively correlated and show relatively high positive loadings on the PCA2, while the capillary water absorption and the contact angles have high loadings on the PCA3 and are negatively correlated (see Figure 2 and Table 3). Accordingly, PCA2 is related to the mechanical strength and PCA3 is related to the behaviour of the mortars in presence of liquid water.

Regarding the objects/samples, the bi-plot of PCA1 and PCA2 (Figure 1) shows a clear separation of the different mortars systems, i.e. limestone cement mortars, natural hydraulic lime mortars and pozzolana lime mortars. The structural properties BD, US, CS, P, TCV distinguish between the natural hydraulic mortars and the limestone cement mortars with the pozzolana-lime mortars. The PCA2 clearly separates the limestone cement mortars from the pozzolana- lime mortars. The samples admixed with the polymer Vinnapas (CMvin0.5,1,1.5) forms a separate group with peculiar pore-structure and mechanical properties, while the CM7301.5 remains isolated.

The bi-plot of PCA2 and PCA3 (Figure 2) does not clearly distinguish between the different mortar systems. The distinction from one mortars to the other is linked to the binder systems on

PCA1 and to the water-repellent admixture used on PCA3. In fact, it is possible to observe that PMA, NMA, CMA (without water-repellents) are located in the upper part of the bi-plot, samples admixed with Silres A® and Sitren P750® are located in the lower part, while the mortars with stearates are in the middle. Furthermore, for each admixture, PCA3 decreases slightly with increasing dosage (e.g. CM7300.5, CM7301, CM7301.5.

To summarize, PCA1 is related to the mortars structure/microstructure, PCA2 is related to the mechanical properties, while PCA3 is related to the hydric behaviour. The microstructure and the mechanical properties allow to differentiate the mortars on the basis of the binder used while PCA3 (that explained 15.38% of the variance) allow to distinguish the mortars on the basis of the water-repellent admixture and its effectiveness.

3.3 PCA of specimens before and after the exposure to salt solution.

Two distinct PCA were performed on data collected on mortar mixtures before and after the exposure to saline solution, Table 4 lists the data averages with respect to the three independent specimens. The PCA are henceforward referred as PCA-before and PCA-after, and the components are named $PC1_{before}$, $PC2_{before}$, $PC1_{after}$, $PC2_{after}$. The first two principal components explained together the 76% and the 77% of the total variance in PCA-before and in PCA-after, respectively (Table 5).

The bi-plot of $PC1_{before}$, $PC2_{before}$ (Table 5 and Figure 3) shows that the variables CS and M/Vi have high negative loadings on $PC1_{before}$, vice versa TCV is negatively correlated. The capillary water absorption has high positive loading on $PC2_{before}$, while the conductivity has negative one. Furthermore, $PC2_{before}$ differentiate between M/V_i and CS. The objects in PCA-before (Figure 3) show a partial separation into different groups mainly according to the different mortar systems although not that clear as for the PCA discussed in paragraph 3.1. The samples without water-repellents PMA's and NMA's seem to form a separate group on the upper part of the bi-plot, having high values of $PC2_{befora,}$ due to their higher capillary water absorption. The projections of the samples with high porosity, low compressive strength and high initial conductivity were located on the left side of the bi-plot.

PCA-after (Table 5 and Figure 4) show a different situation in comparison to PCA-before. The variables CS and M/Vi have high positive loadings on $PC1_{after}$, while C, cond and TCV have negative loadings. C and cond have negative loadings also on $PC2_{after}$, while TCV has positive load on the same component. The projections of the samples on PCA-after show a complex situation (Figure 4): the natural hydraulic lime mortars have low values of $PC1_{after}$ and could be still recognized as a separate group (except NMAs samples), but the pozzolana-lime mortars and limestone cement mortars are overlapped. It can be seen that the mixtures without water repellents (NMA ,PMA, CMA) have low values of both $PC1_{after}$ and $PC2_{after}$, while the mortars added with siloxanes (CMsil, CM750, PMsil, PM750) have high values of $PC1_{after}$. The mortars NM750 and NMsil have higher values of $PC1_{after}$ only in comparison to the other NM mixtures and have also high values on $PC2_{after}$ (high porosity but low water absorption and conductivity).

To summarize, before the exposure $PC1_{before}$ allows to differentiate the samples on the basis of their structural properties and of the binder used, while $PC2_{before}$ allows to distinguish the mortars on the basis of the behaviour in presence of water, therefore on the water-repellent admixture present. After the exposure, M/Vi and CS, C and cond are pairwise correlated: higher capillary absorption determines salt transport inside the mortars, reduces the mechanical strength and the porosity, improves the material loss and the conductivity. Therefore PCA-after allows to differentiate the mixtures on the basis of their resistance to the salt crystallization, which is no more dependent on the mortar binder, but on the water-repellent admixture used. In this specific case higher resistance corresponds to the use of siloxanes.

3.4 Linear mixed modelling of capillary water absorption and mass variation.

3.4.1 Capillary water absorption.

Thereafter, linear mixed effects models are employed to complement PCA results discussed in Section 3.2 through evaluation of the association of the capillary water absorption coefficient C with other properties of the mortars before the exposure to sodium sulphate solution. The data chosen consisted of the measurements of the properties RD, BD, TCV and CS, C on three replicas for each mortar mixture (type NM,CM, PM, without or with siloxanes or stearate at 1% by mass) for a total of 63 samples. Table 2 list the data averaged on the three replicas.

Coefficient C was modelled on the logarithm scale to reduce asymmetry and stabilize variance in this way improving the adherence to the model assumptions. The stepwise model selection procedure supported the model in which variations of C are associated with admixtures and binder type according to the following average relationship:

$\log(C) = 1.63 + 1.72\ \mathrm{NM} - 0.27\ \mathrm{PM} - 3.06\ \mathrm{siloxanes} - 3.91\ \mathrm{stearates}$

where the intercept 1.63 corresponds to the estimated average value of log(C) for binder type CM and no use of admixture. The remaining model coefficients identify additive effects due to specific binder types or the use of admixtures. Further details on estimated model coefficients are reported in Table 6 including standard errors and P-values measuring the significance of estimated model coefficients (P-values lower than 0.05 indicate significant coefficients).

Results indicated that the use of any admixture is associated to a strongly significant reduction of C (siloxanes P=0.003, stearates P=0.007), in this way providing empirical support to the effectiveness of admixtures. The estimated effect of admixture on log(C) is displayed with the *effect plot* on the left panel of Figure 5. The effect plots reported are produced with the R package effects [50]. The estimated mean value of C on the original scale (*i.e.*, not log-transformed) without admixture is 7.76 with 95% predictive interval (1.87, 32.13); 0.36 for siloxanes with 95% predictive interval (0.17, 0.76) and 0.42 for stearates with 95% predictive interval (0.15, 1.15).

As regards the binder type, natural hydraulic lime mortars are associated to higher values of C with respect to limestone cement (P=0.033) while no significant differences are found between limestone cement and pozzolana-lime (P=0.706). See also the effect plot on the right panel of Figure 5. However, P-values indicate that the association between C and binder types is weak.

3.4.2 *Mass variation.*

In order to identify the properties of the mortars which mostly influence the resistance to the action of sodium sulphate solution another linear mixed effects model was developed. The model considers as response variable the percentage mass variation ΔM after four cycle of exposure while the potential predictors are the properties of the mortars measured before the exposure (RD; BD; TCV; CS; C; binder type) on mixtures NM,CM, PM, without or with the admixtures Silres A, Sitren P750, Sitren P730, Tegosivin HE 328, calcium stearates, zinc stearates at 1% by mass (averaged values in Table 2).

The statistical analysis revealed the presence of two outliers (samples CMcast3 and NMSil3 which underwent complete disaggregation) that were removed from the data for model estimation. The presence of fine cracks, not visible at naked eye, on the surfaces may have caused the serious mass losses observed in CMcast3 and NMsil3.

The stepwise model selection procedure supported the model including capillary water absorption C, total cumulative volume TCV and binder type. Instead, admixture, bulk density and compressive strength are rejected from the selected model. The expected value of ΔM according to the selected model is

$$\Delta M = -3.01 - 0.39\ C + 26.39\ TCV - 9.32\ NM - 4.22\ PM.$$

For example, when binder type is CM and C and TCV are equal to their sample mean values of 3.06 and 0.22, respectively, then the estimated mean value of ΔM is $-3.01 - 0.39\ (3.06) + 26.39\ (0.22) = 1.60$. Instead, if the binder type is NM, but C and TCV remains equal to their sample means, then the estimated mean value of ΔM drops to $1.60 - 9.32 = -7.72$. Further details on estimated model components, including p-values, are reported in Table 7. All predictors have P-values around or less than 0.001, thus indicating strong associations. The estimated effects are displayed in Figure 6.

The negative estimated relationships of C with ΔM confirms that the capillary water absorption plays an important role in defining the resistance to the crystallization of salts. High values of C allows the salt solution to deeply penetrate inside the mortars and hence cause damages. However, the precedent linear model (Section 3.4.1), the PCA and the consideration in paragraphs 3.1 highlighted the inverse correlation between C and the effectiveness of the water repellent admixture, thus providing empirical evidence that the use of water-repellent admixtures allowed lower C and better resistance to salt crystallization.

The positive estimated relationships of TCV with ΔM can be related to the possibility, in mortars with high TCV and high pore radius, of hosting larger amounts of salts before suffer serious degradation due to salt crystallization pressure, material spalling and disaggregation. Furthermore, the use of siloxanes admixtures (which demonstrated in most cases high durability) influenced also the TCV, increasing it.

Commentato [UNIVE2]: Aggiungere frase che spieghi come mai l'idrorepellente è in grado di aumentare il volume del sistema. (magari dicendo che la sua presenza sembra agire come stabilizzatore per bolle d'aria durante il mixing

As regards binder type, NM and PM are both associated to a significantly lower level of ΔM than CM. In fact, CM mortars seem to better endure the salt crystallization, thanks probably to a lower capillary absorption and higher compressive strength.

4. Conclusions

The multivariate statistical approach used to study water-repellent mortars greatly simplified the data inspection and the comparison of the different mortar properties. The clear representation of the variables and data in the principal component space helped to evaluate how much properties are influenced by the different mixtures (binding media, water repellent admixtures, etc), demonstrating that PCA can be further applied to the study of physical mortar properties.

Furthermore, linear mixed effects models are an useful tools to relate the effects of a specific environmental condition/ exposure to the starting properties.

The application of PCA to the data collected from different tests on water-repellent mortars hardened for 28 days indicates that the structural and the mechanical properties are correlated and allow to differentiate the mortars into three groups according to the binder used, while the water repellence behaviour is independent and linked to the effectiveness of the water-repellent admixtures.

The PCA on mortars before and after exposure to salt crystallization allows to identify association between structural properties and the resistance to salt solutions and to highlight how the different mortar mixtures were affected by the exposure, visualizing the data in few graphs. In particular the analysis highlighted that the resistance to salt crystallization was mainly due to the possibility of the solution to enter inside the matrix and the mechanical resistance of the mortar mixture. In fact, if the solution is able to enter inside the porous structure, then the mechanical strength and the internal cohesion of the specimens determined the resistance. This second PCA was performed on a reduced number of objects in order to evaluate if it is possible to use this method on exposed samples. Our results indicate that the treatment of physical data regarding weathered mortars might be a promising application of PCA.

The elaboration of linear mixed effects models allowed to obtain an interesting insight of the relationship between the capillary water absorption or the mass variation after four cycles of exposure to salt solutions and the properties and composition of the mortars. The linear mixed models were used to quantify the association between the different factors, which highlighted the predominant importance of the water repellent admixtures used on the capillary water absorption, and of the capillary water absorption (and therefore the admixture), the TCV and the mortar type in determining the resistance to the action of salt solution.

Different environmental conditions require different mortar behaviours. An interesting prospective for future research might be the elaboration linear mixed effects models in order to link the sample composition to specific desirable properties in specific contexts, aiding the development of improved mortar mixtures, suitable in peculiar environmental conditions.

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Tables and Captions

Table 1 Composition of mortar mixtures

Mortar type			**Water repellent admixture**		
	description	**code**	**description**	**code**	**Dosage %**
Portland limestone cement mortar	Binder: CEMII B/L 32.5 Aggregate: silicatic and carbonatic sands (size fraction of 0/1.5) Binder/ aggregate (by volume): 1:3 Water/binder: 0.96	**CM-**	none	**-A**	**0**
			Sitren p750 (powder siloxanes)	**-750-**	**-0.5** **-1** **-1.5**
			Sitren p730 (powder siloxanes)	**-730-**	
			Silres A (powder siloxanes)	**-sil-**	
Natural hydraulic lime mortar	Binder: NHL 3.5 Aggregate: silicatic and carbonatic sands (size fraction of 0/1.2) Binder/aggregate (by volume): 1:3 Water/binder: 0.5	**NM-**	Tegosivin HE (siloxanes in water based emulsion)	**-tes-**	
			Ca Stearate (metal soaps)	**-cast-**	
			Zn stearate (metal soaps)	**-znst-**	
Pozzolana-lime mortar	Binder: Lime+pozzolan 1:1 by volume Aggregate: siliceous sand (size fraction of 0/2) Binder/ aggregate (by volume): 1:3 Water/binder: 1.29	**PM-**	Socal (PCC+ Ca stearates)	**-soc-**	
			Vinnapas 8031 H (polymer)	**-vin-**	

Table 2. The table lists the properties and the samples used for statistical analysis of 28 days hardened mortars. RD, BD, TCV, CS, C, ΔM^{4th} were used for linear mixed effects models.

Mortar mix^1	**RD**	**BD**	**TCV**	**US**	**CS**	**P**	**C**	**a**	**ΔM^{4th}**
	$g\cdot cm^{-3}$	$g\cdot cm^{-3}$	$mm^3\cdot g^{-1}$	$m\cdot s^{-1}$	*Mpa*	$kg\cdot m^2\cdot s^{-1}$	$Kg\cdot m^{-2}h^{-0.5}$	°	%
Limestone cement mortars									
CMA	2.73	1.68	0.167	5397	11.07	61.37*10^{-6}	1.64	w	0.39
CM7500.5	2.73	1.74	0.156	5397	10.51	1.03*10^{-6}	0.06	89	1.19
CM7501	2.73	1.66	0.162	4594	8.25	8.4*10^{-7}	0.18	98	0.79
CM7501.5	2.73	1.66	0.168	4398	8.9	6.5*10^{-7}	0.16	113	0.76
CM7300.5	2.73	1.83	0.143	6129	10.61	9.7*10^{-7}	1.47	35	4.63
CM7301	2.73	1.81	0.141	6821	15.76	6.7*10^{-7}	1.13	61	1.93
CM7301.5	2.73	1.23	0.141	5899	13.31	1.34*10^{-6}	0.81	86	0.60
CMSil0.5	2.73	1.69	0.155	4458	6.83	1.28*10^{-6}	0.23	115	1.20
CMSil1	2.73	1.74	0.174	4172	4.55	9.6*10^{-7}	0.21	108	0.68
CMSil1.5	2.73	1.61	0.157	4430	11.84	9*10^{-7}	0.23	113	1.05
CMtes1	2.73	1.68	0.175	3224	5.34	7.9*10^{-7}	0.11	118	0.13
CMtes5	2.73	1.63	0.17	2510	5	5.4*10^{-7}	0.09	114	0.16
CMcast0.5	2.73	1.77	0.148	7008	16.8	9.7*10^{-7}	1.04	65	3.57
CMcast1	2.73	1.78	0.149	6026	14.56	8.7*10^{-7}	0.47	89	0.91
CMcast1.5	2.73	1.7	0.137	5423	12.23	1.08*10^{-6}	0.38	86	1.17
CMznst0.5	2.73	1.73	0.136	6082	18.3	1.01*10^{-6}	0.48	66	1.80
CMznst1	2.73	1.82	0.141	5996	17.08	1.02*10^{-6}	0.34	80	1.16
CMznst1.5	2.73	1.65	0.161	4226	9.27	1.09*10^{-6}	0.26	97	0.82
CMvin0.5	2.73	1.44	0.252	4949	4.05	2.33*10^{-6}	1.47	49	4.05
CMvin1	2.73	1.44	0.255	4917	3.77	1.61*10^{-6}	1.42	82	6.29
CMvin1.5	2.73	1.42	0.259	4593	4.4	1.81*10^{-6}	1.23	74	7.00
Natural hydraulic lime mortars									
NMA	2.74	1.53	0.34	1105	1.32	2.16*10^{-6}	11.9	w	-10.45
NM7500.5	2.74	1.46	0.38	1082	0.34	2.14*10^{-6}	1.29	100	-7.98
NM7501	2.74	1.18	0.45	1114	0.89	2.02*10^{-6}	0.24	120	-0.14
NM7300.5	2.74	1.5	0.34	1153	0.41	1.51*10^{-6}	1.45	70	^{d}

Mortar mix[1]	RD	BD	TCV	US	CS	P	C	a	ΔM^{4th}
	$g\cdot cm^{-3}$	$g\cdot cm^{-3}$	$mm^3\cdot g^{-1}$	$m\cdot s^{-1}$	*Mpa*	$kg\cdot m^2\cdot s^{-1}$	$Kg\cdot m^{-2}h^{-0.5}$	°	%
NM7301	2.74	1.32	0.35	1096	0.74	$2.18*10^{-6}$	0.44	80	-1.70
NMSil0.5	2.74	1.46	0.33	1080	0.57	$2.06*10^{-6}$	2.61	w	-24.00
NMSil1	2.74	1.18	0.39	1078	0.83	$2.33*10^{-6}$	0.33	125	-6.46
NMcast0.5	2.74	1.41	0.4	1075	0.84	$1.69*10^{-6}$	2.09	w	-25.50
NMcast1	2.74	1.21	0.41	1105	0.62	$2.32*10^{-6}$	1.01	w	-8.17
NMznst0.5	2.74	0.95	0.33	1227	1.47	$1.9*10^{-6}$	0.91	w	-22.82
NMznst1	2.74	1.35	0.28	1278	0.62	$1.65*10^{-6}$	0.2	80	-4.56
NMsoc0.5	2.74	1.42	0.4	1029	1.06	$1.7*10^{-6}$	2.65	w	-33.32
NMsoc1	2.74	1.17	0.42	1048	0.55	$2.19*10^{-6}$	1.94	w	-21.95
Pozzolana-lime mortars									
PMA	2.6	1.77	0.133	1205	2	$6*10^{-7}$	20	w	-8.42
PM7501	2.6	1.44	0.214	1160	1.07	$8*10^{-7}$	0.049	130	-0.30
PM7301	2.6	1.69	0.136	1180	1.2	$7*10^{-7}$	6	w	-11.22
PMsil0.5	2.6	1.55	0.148	1170	1.73	$8.4*10^{-7}$	0.78	128	-1.23
PMsil1	2.6	1.57	0.16	1150	2.24	$5.6*10^{-7}$	0.045	130	-0.34
PMsil1.5	2.6	1.56	0.149	1130	2.04	$5.1*10^{-7}$	0.058	143	-0.76
PMtes1	2.6	1.65	0.155	1008	0.89	$6.5*10^{-7}$	0.071	126	-0.58
PMcast0.5	2.6	1.74	0.119	1075	2.35	$5.8*10^{-7}$	1.9	w	-10.99
PMcast1	2.6	1.73	0.128	1225	2	$5.1*10^{-7}$	0.252	w	-5.61
PMcast1.5	2.6	1.71	0.134	1227	2.06	$5.6*10^{-7}$	0.14	w	-1.64
PMznst0.5	2.6	1.72	0.148	1002	0.6	$9.6*10^{-7}$	0.101	w	[d]
PMznst1	2.6	1.75	0.148	998	0.26	$9.8*10^{-7}$	0.067	118	-3.91
PMznst1.5	2.6	1.71	0.148	1000	0.05	$9.8*10^{-7}$	0.05	126	d

[1] RD Real density; BD bulk density; TCV total cumulative volume; US ultrasonic measurements; CS compressive strength; P water vapour permeability; C capillary water absorption; a contact angle; ΔM^{4th} mass variation after four salt cycles. W= completely wettable; [d]= completely disaggregated

Table 3 PCA analysis of 28 days hardened mortars. Loadings for the first three components. The bold text underlines variable with loads higher than 0.4 on the relative component.

Variables		1st Component (43%)*	2nd Component (26%)*	3rd Component (17%)*
RD	real density	-0.14	**0.61**	0.13
BD	bulk density	**0.46**	-0.13	0.21
TCV	total cumulative volume MIP	**-0.51**	0.16	-0.04
US	ultrasonic measurements	0.35	**0.50**	0.11
CS	compressive strength	0.38	**0.44**	0.14
P	water vapour permeability	**-0.46**	0.30	0.03
C	capillary water absorption coefficient	-0.09	-0.21	**0.67**
a	contact angle	0.18	0.04	**-0.67**

* percentage of variance explained by each component

Table 4 The table lists the properties and the samples used for the PCA analysis of water repellent mortars before and after the immersion cycles in saturated sodium sulphate solution. TCV Total cumulative volume MIP ; CS compressive strength; C Capillary water absorption; cond Conductivity 0.5-1.0 cm depth; M/Vi mass / starting volume

	TCV	CS	C	cond	M/V_i
Mix name	$mm^3\cdot g^{-1}$	*Mpa*	$Kg\cdot m^{-2}h^{-0.5}$	$\mu s\cdot cm^{-1}$	$g\cdot cm^{-3}$
Before the immersion cycles in saturated sodium sulphate solution					
CMA	0.167	11.07	1.64	70	1.63
CM7501	0.162	8.25	0.18	71	1.65
CMSil1	0.174	4.55	0.21	69	1.62
CMcast1	0.149	14.56	0.47	85	1.73
NMA	0.340	1.32	11.90	83	1.53
NM7501	0.450	0.89	0.24	108	1.18

NMSil1	0.390	0.83	0.33	84	1.18
NMcast1	0.410	0.62	1.01	91	1.21
PMA	0.133	2.00	20.01	71	1.71
PM7501	0.214	1.07	0.05	85	1.52
PMsil1	0.160	2.24	0.05	51	1.60
PMcast1	0.128	2.01	0.25	102	1.65
After the immersion cycles in saturated sodium sulphate solution					
CMA	0.200	0.01	2.63	101	1.18
CM7501	0.180	4.91	0.12	114	1.65
CMSil1	0.200	3.68	0.12	120	1.63
CMcast1	0.160	3.38	1.46	121	1.29
NMA	0.280	0.12	19.95	101	1.37
NM7501	0.430	0.30	0.45	114	1.18
NMSil1	0.450	0.21	10.26	126	1.09
NMcast1	0.420	0.12	3.63	137	1.11
PMA	0.140	0.01	19.56	210	1.07
PM7501	0.170	0.71	0.07	81	1.52
PMsil1	0.180	1.45	0.04	58	1.59
PMcast1	0.140	0.37	3.64	235	1.45

Table 5 PCA analysis of mortars before and after the exposure to salt solution. Loadings for the first three components. The bold text underlines variable with loadings higher than 0.4 on the relative component.

Variables		PCA-before		PCA-after	
		1st Component (52%)*	2nd Component (76%)*	1st Component (49%)*	2nd Component (28%)*
TCV	total cumulative volume MIP	**0.57**	0.00	-0.22	**0.75**
CS	compressive strength	**-0.44**	-0.36	**0.53**	-0.15
C	Capillary water absorption coefficient	0.12	0.81	**-0.47**	-0.29
cond	Conductivity of the first 0.5-1.0 cm	0.37	**-0.42**	-0.38	**-0.55**
M/V_i	Degradation parameter	**-0.57**	0.19	**0.56**	-0.18

* Percentage of variance explained by each component

Table 6: Estimated parameters (Est.), standard errors (SE) and p-values of the selected linear mixed effects model for log(C). The intercept parameter corresponds to binder type CM and no use of admixture.

Parameters	**Est.**	**SE**	**P-value**
intercept	1.63	0.86	0.066
type NM	1.72	0.73	0.033
type PM	-0.27	0.7	0.706
siloxanes	-3.06	0.85	0.003
stearates	-3.91	0.93	0.007

Table 7: Estimated parameters (Est.), standard errors (SE), and p-values of the selected linear mixed effects model for ΔM. The intercept parameter corresponds to binder type CM.

Parameters	**Est.**	**SE**	**P-value**
Intercept	-3.01	1.37	0.035
TCV	26.39	7.12	0.001
type NM	-9.32	1.94	<0.001
type PM	-4.22	1.15	0.002
C	-0.39	0.09	<0.001

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