

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

Laura Falchi<sup>a\*</sup>, Cristiano Varin<sup>a</sup>, Giuseppa Toscano<sup>a</sup>, Elisabetta Zendri<sup>a</sup>

<sup>a</sup>Department of Environmental Sciences, Informatics and Statistics, Ca' Foscari University of Venice; Via Torino 155 B, 30170, Mestre (Venice), Italy; Phone +39 041 2346732; laura.falchi@stud.unive.it; sammy@unive.it; toscano@unive.it; elizen@unive.it

**\*Corresponding Author.**

Laura Falchi

Department of Environmental Sciences, Informatics and Statistics, Ca' Foscari University of Venice; Via Torino 155 B, 30170, Mestre (Venice); Italy  
Phone +39 041 2346732  
laura.falchi@stud.unive.it

**Article Type: Research Paper**

**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<sub>2</sub> 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

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

14 This paper proposes a methodological approach based on multivariate statistical techniques such  
15 as PCA and linear mixed effects models [35] to study both the properties of water repellent  
16 mortars and the effects of the exposure to salt solutions. The statistical methods were used in the  
17 attempt to: i) classify the water repellent mortar samples in more or less distinct groups,  
18 depending on their physical and structural characteristics; ii) highlight the different behaviour due  
19 to the weathering processes, in particular of samples exposed to the action of damaging salt  
20 solutions; iii) evaluate how different physical characteristics, such as the mortar composition,  
21 their strength, porosity, water absorption, can influence the durability and in particular the  
22 resistance to salt crystallization.

23 The data for the statistical elaborations were collected on hydraulic mortars with water-repellent  
24 properties, suitable for the restoration of historical buildings. Natural hydraulic lime, pozzolana-  
25 lime and limestone cement were used as binders, while water-repellent admixtures were selected  
26 between those most commonly used, namely, calcium and zinc stearate, powder silane/siloxane  
27 and silane water-based emulsions. Some of the water-repellent mortars, after one year of  
28 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 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® (Ceraio di Dolc , Italy); a mixture of industrial lime hydrate (by BASF®) and the S&B -silica®, a pozzolana of volcanic origin from Greece.

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 (  40-130 nm) coated by calcium stearate. The complete list of the specimens and their composition is listed in Table 1.

**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.

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 ( $145 \pm 10$ ) rpm, then, water was poured on the dry components and the obtained mixture was worked for 3 minutes ( $285 \pm 10$ ) 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<sup>3</sup>, demoulded after 2 days, and 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<sup>3</sup> or slices ( $2 \times 4 \times 4$ ) cm<sup>3</sup>. 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  $\Delta M$  of the 4<sup>th</sup> cycle was chosen in order to compare the effects for mortars with different binders, before the complete disaggregation of some of the specimens.

## 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: s

Eliminato: structural

1 The structure was evaluated through measurements of : bulk density BD of hardened mortar  
2 prisms; real density RD (measured on grinded samples with a Micromeritics 1305 multivolume  
3 helium pycnometer); total cumulative volume of mercury intruded (TCV) linked to the total open  
4 porosity with a ThermoQuest/Finningam Pascal 140 and Pascal 240 mercury porosimeter MIP  
5 [39; 40]. In order to provide further information regarding the structure with a non-destructive  
6 evaluation, ultrasonic measurements US were done on prismatic specimens with a Controls 58-  
7 E4800 UPV with standard piezoelectric sensor at 45 Hz (cylinder 5cm Ø X5cm h), pulse rate 2 s,  
8 resolution 0.1µs. A direct configuration of the measurements, e.g. transmitter and receiver at the  
9 opposite sides of the specimens, was done along the longitudinal and transverse axes [41].  
10 The compressive strength CS was measured with a Zwick/Roell Z010 press (pre-load 20 N,  
11 loading rate 50N/s) on prismatic samples according to UNI EN 12390-5:2009 [42].  
12 Properties related to the behaviour in respect to water and water vapour such as water vapour  
13 permeability (P) [43,44], capillary water absorption coefficient C [45], surface wettability a  
14 (determination of contact angle according to NorMAL 33/89 with a Data Phisic ETT/XL  
15 instrument [46]) were measured too. The ionic conductivity of the samples was measured to  
16 evaluate the total soluble salt content as described by Normal 13/83 [47] on samples collected  
17 from the specimens at a 0.5-1 cm depth.

**Eliminato:** and bulk density (BD MIP) both

18

## 19 **2.4 Principal component analysis**

20 Among the multivariate statistical methods, PCA was chosen in order to achieve a reduction of  
21 dimensionality, thus allowing an easier visualization of the relationships between the parameters.  
22 The interpretation of the analysis allows also to evaluate the presence of mortars with similar  
23 behavior. The statistical software R [48] was used to elaborate the data. Given the different scales  
24 of measurement, PCA has been performed on the correlation matrix.  
25 A first PCA was performed on the data collected on 28 day's hardened mortars. The physical  
26 parameter used as variables for this PCA were: i) physical and structural properties of the  
27 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  $\alpha$  (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  $\Delta M$  (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  $\Delta M$ , can be approximatively described as a linear combination of a set of explicative 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  $i$  ( $i = 1, \dots, 20$ ) and specimen  $j$  ( $j = 1, 2, 3$ ), and let  $x_{1,ij}, \dots, x_{p,ij}$  be  $p$  explicative variables. Then, the linear mixed model with random intercept is:

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

1 where  $\beta_0$  is the model intercept,  $\beta_1, \dots, \beta_p$  are the coefficients measuring the contribution of  
 2 the explicative variables,  $\mu_i$  is the random intercept that accounts for the departures from the  
 3 expected value due to the specific sample  $i$  and  $\varepsilon_{ij}$  is an error term. Model parameters are  
 4 estimated under traditional distributional assumptions, namely random intercepts  $\mu_i$  assumed to be  
 5 realizations of independent normal variables with zero mean and variance  $\sigma^2$ , and errors  $\varepsilon_{ij}$   
 6 assumed to be realizations of independent normal variables with zero mean and variance  $\tau^2$ .  
 7 Furthermore, random intercepts are assumed to be mutually independent of error terms.  
 8 The capillary water absorption  $C$  should be linked to the admixtures effectiveness and should  
 9 influence also the durability in different environmental conditions, therefore we consider the  
 10 study of the variables associated to  $C$  is of particular interest in order to evaluate the durability of  
 11 the mortars.  
 12 The mass variation  $\Delta M$  is another simple parameter that can be used in order to evaluate the  
 13 effects of the exposure: positive mass variation can be linked to the formation of salts inside the  
 14 mortar structure, negative mass variation can be linked to material decohesion and losses due to  
 15 specimens degradation.  
 16 Linear mixed effects models were developed on the available data consisting in 20 samples, type  
 17 CM, NM or PM with the admixtures Silres A, Sitren P750, Sitren P730, Tegosivin HE 328,  
 18 Calcium stearates, zinc stearates at 1% by mass, formed by three specimens each. The model used  
 19 to identify variables associated to  $C$  include as potential explicative variables the compressive  
 20 strength  $CS$ , the total cumulative volume  $TCV$ , the real density  $RD$ , and factors linked to the  
 21 mortar composition (binder type PM pozzolana-lime, CM limestone cement, NM natural  
 22 hydraulic lime mortars) and admixtures (siloxanes, stearates or none). Models for  $\Delta M$  employ the  
 23 same potential explicative variables with the addition of  $C$ .  
 24 Models are fitted with the maximum likelihood method as implemented in the R package nlme  
 25 [49]. Model selection is based on a stepwise procedure using the Akaike Information Criterion  
 26 (AIC). Validity of model assumptions is assessed through graphical inspection of residuals.  
 27



### 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  $M/V_i$  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  $PC2_{before}$ , 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<sub>after</sub>, while C, cond and TCV have negative loadings. C and cond have negative loadings also on PC2<sub>after</sub>, 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<sub>after</sub> 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<sub>after</sub> and PC2<sub>after</sub>, while the mortars added with siloxanes (CMSil, CM750, PMSil, PM750) have high values of PC1<sub>after</sub>. The mortars NM750 and NMSil have higher values of PC1<sub>after</sub> only in comparison to the other NM mixtures and have also high values on PC2<sub>after</sub> (high porosity but low water absorption and conductivity). To summarize, before the exposure PC1<sub>before</sub> allows to differentiate the samples on the basis of their structural properties and of the binder used, while PC2<sub>before</sub> 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:

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

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  $\Delta M$  after four cycle of exposure

1 while the potential predictors are the properties of the mortars measured before the exposure (RD;  
 2 BD; TCV; CS; C; binder type) on mixtures NM, CM, PM, without or with the admixtures Silres  
 3 A, Sitren P750, Sitren P730, Tegosivin HE 328, calcium stearates, zinc stearates at 1% by mass  
 4 (averaged values in Table 2).  
 5 The statistical analysis revealed the presence of two outliers (samples CMcast3 and NMSil3  
 6 which underwent complete disaggregation) that were removed from the data for model  
 7 estimation. The presence of fine cracks, not visible at naked eye, on the surfaces may have caused  
 8 the serious mass losses observed in CMcast3 and NMSil3.  
 9 The stepwise model selection procedure supported the model including capillary water absorption  
 10 C, total cumulative volume TCV and binder type. Instead, admixture, bulk density and  
 11 compressive strength are rejected from the selected model. The expected value of  $\Delta M$  according  
 12 to the selected model is  
 13  $\Delta M = -3.01 - 0.39 C + 26.39 TCV - 9.32 NM - 4.22 PM$ .  
 14 For example, when binder type is CM and C and TCV are equal to their sample mean values of  
 15 3.06 and 0.22, respectively, then the estimated mean value of  $\Delta M$  is  $-3.01 - 0.39 (3.06) + 26.39$   
 16  $(0.22) = 1.60$ . Instead, if the binder type is NM, but C and TCV remains equal to their sample  
 17 means, then the estimated mean value of  $\Delta M$  drops to  $1.60 - 9.32 = -7.72$ . Further details on  
 18 estimated model components, including p-values, are reported in Table 7. All predictors have P-  
 19 values around or less than 0.001, thus indicating strong associations. The estimated effects are  
 20 displayed in Figure 6.  
 21 The negative estimated relationships of C with  $\Delta M$  confirms that the capillary water absorption  
 22 plays an important role in defining the resistance to the crystallization of salts. High values of C  
 23 allows the salt solution to deeply penetrate inside the mortars and hence cause damages. However,  
 24 the precedent linear model (Section 3.4.1), the PCA and the consideration in paragraphs 3.1  
 25 highlighted the inverse correlation between C and the effectiveness of the water repellent  
 26 admixture, thus providing empirical evidence that the use of water-repellent admixtures allowed  
 27 lower C and better resistance to salt crystallization.

The positive estimated relationships of TCV with  $\Delta M$  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.

As regards binder type, NM and PM are both associated to a significantly lower level of  $\Delta M$  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

**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

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.

## Acknowledgments

Special thanks are due to Ph.D. Engineer Urs Müller and to BAM institute of Berlin for their help with the characterization of pozzolana-lime samples. Many thanks to Ca Foscari University who funded this work.

## Bibliography

- [1] Winkler EM. Stone: properties, durability in man's environments, Wien, 1975.
- [2] Wendler E, Charola AE. Water and its Interaction with Porous Inorganic Building Materials. In: Hydrophobe V, Water repellent treatment of building materials. Freiburg: Aedificatio Publisher; 2008, p. 57-74.
- [3] Amoroso G, Fassina V. Stone Decay and Conservation: Atmospheric Pollution, Cleaning, Consolidation and Protection, London: Elsevier Science Ltd, 1983.
- [4] Driussi G, Valle A, Biscontin G. Porosity and soluble salts as decay parameters of stone materials, In: "V International Congress on Deterioration and Conservation of Stone", Lausanne; 1985, p. 25-27.
- [5] Verhoef LGW. Water-AParadox, the prerequisite of Life but the Cause of Decay. In: Hydrophobe III Surface technology with Water Repellent Agents. Freiburg: Aedificatio Publisher; 2001, p. 21-36.
- [6] Carmona-Quiroga PM, Martínez-Ramírez S, Sánchez de Rojas MI, Blanco-Varela MT. Surface water repellent-mediated change in lime mortar colour and gloss. Constr Build Mater 2010; 24 (11): 2188-2193.
- [7] Urzì C, De Leo F. Evaluation of the efficiency of water-repellent and biocide compounds against microbial colonization of mortars, Int Biodeter Biodegr 2007; 60 (1): 25-34.

- [8] Domingo C, Alvarez de Buergo M, Sánchez-Cortés S, Fort R, García-Ramos JV, Gomez-Heras M. Possibilities of monitoring the polymerization process of silicon-based water repellents and consolidants in stones through infrared and Raman spectroscopy. *Prog Org Coat* 2008; 63 (1): 5-12.
- [9] Jian-Guo Dai, Akira Y, Wittmann FH, Yokota H, Zhang P. Water repellent surface impregnation for extension of service life of reinforced concrete structures in marine environments: The role of cracks, *Cement Concrete Comp* 2010; 32 (2): 101-109. <http://dx.doi.org/10.1016/j.cemconcomp.2009.11.001>.
- [10] Falchi L, Müller U, Fontana P, Izzo F.C, Zendri E. Influence and effectiveness of water-repellent admixtures on pozzolana-lime mortars for restoration application. *Constr Build Mater* 2013; 49: 272-280.
- [11] Izaguirre A, Lanas J. Effect of water-repellent admixtures on the behaviour of aerial lime based-mortars, *Cement Concrete Res* 2009; 39:1095-1104.
- [12] Izaguirre A, Lanas J, Álvarez J. Ageing of lime mortars with admixtures: Durability and strength assessment. *Cement Concrete Res* 2010; 40: 1081-1095.
- [13] Zhang P, Wittmann FH, Zhao TJ. Observation and quantification of water penetration into strain Hardening Cement-based Composites (SHCC) with multiple cracks by means of neutron radiography. *Nucl Instrum Methods* 2010; A260:414-420.
- [14] Lanzon M, Garcia-Ruiz PA. Evaluation of capillary water absorption in rendering mortars, made with powdered waterproofing additives. *Constr Build Mater* 2009; 23: 3287-3291.
- [15] Aberlee T, Emmenegger P, Vallee F. New Approaches to Increase Water Resistance of Gypsum Based Building Materials. Proceedings of the conference "Drymix Mortar Yearbook 2010". 2010.
- [16] Barreca F, Fichera CR. Use of olive stone as an additive in cement lime mortar to improve thermal insulation. *Energ Buildings* 2013; 62: 507-513.
- [17] Li W, Wittman FH, Jiang R, Zhao T, Wolfseher R. Metal soaps for the production of integral Water repellent Concrete, In: Borelli E, Fassina V. editors. *Hydrophobe VI*, 6<sup>th</sup> international conference on water repellent treatment of building materials, Freiburg: Aedificatio Publisher 2011, p. 145-154.
- [18] Lanzón M, Garcia Ruiz PA. Effectiveness and durability evaluation of rendering mortars made with metallic soaps and powdered silicone. *Constr Build Mater* 2008; 22: 2308-2315.
- [19] Roos M, König F, Stadtmüller S, Weyershausen B. Evolution of Silicone based Water Repellents for Modern Building Protection. In: *Hydrophobe V*, Water repellent treatment of Building materials. Freiburg: Aedificatio Publisher; 2008.
- [20] Pacheco F, Faria J, Jalali S. Some consideration about the use of lime-cement mortars for building conservation purposes in Portugal: A reprehensible option or a lesser evil?. *Constr Build Mater* 2012; 30: 488-494.
- [21] Papayianni I, Pachta V, Stefanidou M. Analysis of ancient mortars and design of compatible repair mortars: The case study of Odeion of the archaeological site of Dion. *Constr Build Mater* 2013; 40: 84-92.
- [22] Marvelaki-Kalaitzaki P, Agioutantis Z, Lionakis E, Stavroulaki M, Perdikatsis V. Physico-chemical and mechanical characterization of hydraulic mortars containing nano-titania for restoration applications, *Cement Concrete Comp* 2013; 36: 33-41.
- [23] Moropoulou A, Bakolas A, Moundoulas P. Criteria and methodology for restoration mortars compatible to the historic materials and structures. In: *Proceedings of the 9th international congress on deterioration and conservation of stone*. Venice; 2000, p. 403-412.
- [24] World Business Council for Sustainable Development (WBCSD) and International Energy Agency (IEA). *Cement Technology Roadmap 2009, carbon emissions reductions up to 2050*. Switzerland, 2009 [online] <http://www.wbcsdcement.org/>
- [25] Cardell, C., F. Delalieux, K. Roumpopoulos, A. Moropoulou, F. Auger, R. Van Grieken. Salt induced decay in calcareous stone monuments and buildings in a marine environment in SW France, *Constr Build Mater* 2003; 17: 165-179.
- [26] Potgieter-Vermaak SS, Potgieter JH, Worobiec A, Van Grieken R, Marjanovic L, Moeketsi S. Fingerprinting of South African ordinary Portland cements, cement blends and mortars for identification purposes. Discrimination with starplots and PCA, *Cement Concrete Res* 2007; 37 (6): 834-843.
- [27] Musumarra G, Stella M, Matteini M, Rizzi M. Multiariate characterization, using the SIMCA method, of mortars from two frescoes in Chiaravalle Abbey, *Thermochimica Acta* 1995; 269-270:797-807.
- [28] Moropoulou A, Polikreti K, Bakolas A, Michailidis P. Correlation of physicochemical and mechanical properties of historical mortars and classification by multivariate statistics. *Cement Concrete Res* 2003; 33 (6): 891-898.
- [29] Rampazzi L, Pozzi A, Sansonetti A, Toniolo L, Giussani B. A chemometric approach to the characterisation of historical mortars. *Cement Concrete* 2006; 36 (6): 1108-1114.



- [30] Arizio E, Piazza R, Cairns WRL, Appolonia L, Botteon A. Statistical analysis on ancient mortars: A case study of the Balivi Tower in Aosta (Italy). *Constr Build Mater* 2013; 47: 1309-1316.
- [31] Esbensen KH, Geladi P. 2.13 - Principal Component Analysis: Concept, Geometrical Interpretation, Mathematical Background, Algorithms, History, Practice, In: Brown SD, Tauler R, Walczak B, editors. *Comprehensive Chemometrics*. Oxford: Elsevier; 2009, p. 211-226.
- [32] F. Wang, Factor Analysis and Principal-Components Analysis, In: Editors-in-Chief: Rob Kitchin and Nigel Thrift, Editor(s)-in-Chief, *International Encyclopedia of Human Geography*, Elsevier, Oxford, 2009, Pages 1-7
- [33] G. Scarponi, C. Turetta, G. Capodaglio, G. Toscano, C. Barbante, I. Moret, P. Cescon, Chemometric studies in the lagoon of venice, Italy 1. The environmental quality of water an sediment matrices, *journal of chimica information and computer science j.Chem.Inf.Comput.Sci.*,1998, volume 38, number 4, pages 552,562.
- [34] Barbera G, Barone G, Mazzoleni P, Scandurra A. Laboratory measurement of ultrasound velocity during accelerated aging tests: Implication for the determination of limestone durability, *Constr Build Mater* 2012; 36:977-983. <http://dx.doi.org/10.1016/j.conbuildmat.2012.06.029>.
- [35] Laird NM, Ware JH. Random-Effects Models for Longitudinal Data. *Biometrics* 1982; 38: 963-974.
- [36] EN 12370 Natural Stone Test Methods - Determination of Resistance to Salt Crystallisation. European Committee for Standardization
- [37] EN 459-1: 2002 Building lime Definitions, specifications and conformity criteria. European Committee for Standardization. ([n.b. the NHL was produced before the EN 459-1: 2010 came into force](#))
- [38] EN 196-1:2005 Methods of testing cement - Part 1: Determination of strength. European Committee for Standardization.
- [39] CNR-ICR NorMaL 4/80 Distribuzione del Volume dei Pori in Funzione del loro Diametro (Italian normative on stone material-Distribution of pores volume vs. their diameter). Commissione Beni Culturali UNI NorMaL
- [40] Instruction Manual Porosimeter PASCAL 240, CE Instruments, P/N 317 13028, Rev. C3-PM4-12/96, Mila; 1996, Section 1, p 6.
- [41] Molero Armenta, M., I. Segura, M. Hernandez, M.A. Garcia Izquierdo, J. Anaya, Ultrasonic characterization of cementitious materials using frequency-dependent velocity and attenuation, NDTCE'09, Non-Destructive Testing in Civil Engineering, Nantes, France, June 30th – July 3rd, 2009
- [42] EN 12390-3:2009 Testing hardened concrete. Compressive strength of test specimens. European Committee for Standardization.
- [43] EN 1015-19, Methods of Test for Mortar for Masonry - Part 19: Determination of Water Vapour Permeability of hardened Rendering and Plastering Mortars
- [44] DIN 52615 Testing of thermal insulating materials; Determination of water vapour permeability of construction and insulating materials
- [45] EN 1015-18:1999 Methods of Test for Mortar for Masonry - Part 18: Determination of Water Absorption Coefficient due to Capillary Action of hardened Rendering Mortar. European Committee for Standardization.
- [46] CNR-ICR NorMaL 33/89 Misura dell'angolo di contatto (Italian normative on stone material-Contact angle measurement). Commissione Beni Culturali UNI NorMaL.
- [47] CNR- ICR NorMaL 13/83 Dosaggio dei sali solubili totali mediante misure di conducibilità (Italian normative on stone material- Determination of the content of soluble salts with conductivity measurements).
- [48] R Core Team. R: A language and environment for statistical computing. R Foundation for Statistical Computing, Wien Austria; 2014. URL <http://www.R-project.org/>.
- [49] Pinheiro J, Bates D, DebRoy S, Sarkar D and the R Development Core Team. nlme: Linear and Nonlinear Mixed Effects Models. R package version 3.1-117. 2014
- [50] Fox J. Effect Displays in R for Generalised Linear Models. *J Stat Software* 2003; 8(15): 1-27. URL <http://www.jstatsoft.org/v08/i15/>.

## 1 Tables and Captions

2 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-	

3  
4 Table 2. The table lists the properties and the samples used for statistical analysis of 28 days  
5 hardened mortars. RD, BD, TCV, CS, C,  $\Delta M^{4th}$  were used for linear mixed effects models.

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

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

<sup>1</sup>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<sup>4th</sup> mass variation after four salt cycles. W= completely wettable; <sup>d</sup>= 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		1 <sup>st</sup> Component (43%)*	2 <sup>nd</sup> Component (26%)*	3 <sup>rd</sup> Component (17%)*
<b>RD</b>	real density	-0.14	<b>0.61</b>	0.13
<b>BD</b>	bulk density	<b>0.46</b>	-0.13	0.21
<b>TCV</b>	total cumulative volume MIP	<b>-0.51</b>	0.16	-0.04
<b>US</b>	ultrasonic measurements	0.35	<b>0.50</b>	0.11
<b>CS</b>	compressive strength	0.38	<b>0.44</b>	0.14
<b>P</b>	water vapour permeability	<b>-0.46</b>	0.30	0.03
<b>C</b>	capillary water absorption coefficient	-0.09	-0.21	<b>0.67</b>
<b>a</b>	contact angle	0.18	0.04	<b>-0.67</b>

\* 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/V<sub>i</sub> mass / starting volume**

Mix name	TCV $mm^3 \cdot g^{-1}$	CS Mpa	C $Kg \cdot m^{-2} h^{0.5}$	cond $\mu s \cdot cm^{-1}$	M/V <sub>i</sub> $g \cdot cm^{-3}$
<i>Before the immersion cycles in saturated sodium sulphate solution</i>					
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
<i>After the immersion cycles in saturated sodium sulphate solution</i>					
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	
	1 <sup>st</sup>	2 <sup>nd</sup>	1 <sup>st</sup>	2 <sup>nd</sup>
	Component (52%)*	Component (76%)*	Component (49%)*	Component (28%)*
<b>TCV</b> total cumulative volume MIP	<b>0.57</b>	0.00	-0.22	<b>0.75</b>
<b>CS</b> compressive strength	<b>-0.44</b>	-0.36	<b>0.53</b>	-0.15
<b>C</b> Capillary water absorption coefficient	0.12	0.81	<b>-0.47</b>	-0.29
<b>cond</b> Conductivity of the first 0.5-1.0 cm	0.37	<b>-0.42</b>	-0.38	<b>-0.55</b>
<b>M/V<sub>i</sub></b> Degradation parameter	<b>-0.57</b>	0.19	<b>0.56</b>	-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  $\Delta M$ . 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