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Artificial weathering of water-repellent mortars suitable for restoration applications

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SUMMARY: The study evaluates Portland limestone cement mortars, natural hydraulic lime mortars and pozzolan-lime mortars modified with water-repellent admixtures (metal soaps and siloxanes) for their use in the maintenance of historic buildings. The chemical-physical characteristics, the durability and the resistance to artificial weathering (exposure to UV light and artificial rain) were examined. The exposure conditions used in the ageing test were chosen in order to simulate outdoor environmental conditions, in particular the processes caused by UV-light and thermal shock induced by rain water.

KEY-WORDS: water repellent admixtures, mortars, Portland limestone cement, natural hydraulic lime, pozzolana-lime, artificial weathering

INTRODUCTION

Over the last years the use of water repellent admixtures to produce in-bulk water repellent mortars has been proposed and studied in order to address the problem of the protection of architectonic surfaces from the degradation processes linked to the water action [1-4].

Water repellent admixtures based on siloxanes or metal soaps are commonly and widely used in cement-based mortars and renders, but have been less studied for application in the restoration field [5, 6], where the use of ordinary Portland cement may not be compatible with historical building materials. The requirements of reliable and durable solutions to repair historical structures without causing new damages, led to the choice of materials, which are compatible with the historical ones, such as pozzolan-lime, lime or natural hydraulic lime binders. The demand for more sustainable solutions has resulted in the development and study of construction materials with a lower environmental impact, such as blended cements or other kinds of hydraulic limes [7, 8].

In this contribution, organo-silicon compounds and metal soaps were added to mortars with Portland limestone cement, natural hydraulic lime and pozzolan-lime in order to obtain water repellent properties adjusted to restoration interventions. The aim of this study was to investigate the effect of the admixtures on the mortar properties and the behavior and durability of water repellent mortars exposed to UV radiation, rain and thermal shocks.

EXPERIMENTAL

Preparation of water-repellent mortars

Water-repellent mixes were prepared using three different binders and three sands. Different powder organosilicon compounds and metal soaps were added as water-repellent admixtures.

- Portland limestone composite cement CEM II/B-L 32.5 R supplied by CementiRossi® (Pederobba, Italy) was mixed with a carbonate-siliceous sand with a size fraction of (0/1.5) in a 1:4.1 by mass ratio (volume ratio 1:3), and a water-binder ratio w/b of 0.9 was used;
- Natural hydraulic lime NHL3.5 "Calce dei berici" supplied by Villaga S.p.A. (Verona, Italy) was mixed with a carbonate-siliceous sand with a size fraction of (0/1.2) in a 1:5.1 (1:3 by volume ratio), w/b of 0.5;
- Pure calcium hydroxide supplied by BASF® was mixed with the Greek pozzolan S&Bμ-silica® supplied by S&B Industrial minerals in a 1:1 by mass ratio to obtain a binder, which was then mixed with a CEN standard sand [9] as aggregate (size fraction of 0/2) in a 1:7 by mass ratio (1:3 volume ratio) binder/aggregates, w/b of 1.3.

To obtain the water-repellent mortars, to each binder-aggregate system a 1 % by weight of the water repellent admixtures was added. The water repellent admixtures were powder products based on alkylpolysiloxanes Sitren P750, and Sitren P730 from Evonik®; calcium stearate and zinc stearate from Sigma Aldrich®. The water repellent percentage was chosen considering previously published data [1, 2]. Mortars prepared without water-repellent admixtures were used as reference mixtures. The denotations of the specimens and their composition are summarized in Table 1.

Sample preparation (mixing, demoulding and curing) were done according to EN 196-1 [9]. The powder materials were mixed in a planetary mixer at low speed (145 ±10) rpm for 3 minutes, then, water was added and the obtained mixtures were worked for 3 minutes (285 ±10) rpm. The mixtures were then poured in polystyrene moulds for obtaining prisms (40 x 40 x 160 mm^3), demoulded after 2 days, and stored at RH = 90% and T= 23 ±2 °C for 28 days. The specimens were cut with a diamond saw in order to obtain cubes (40 x 40 x 40 mm^3).

Artificial weathering of water-repellent mortars

Artificial weathering was performed on cubes in order to simulate the deterioration processes caused by sunlight, water and temperature variations following the indications of EN 13687 "Thunder-shower cycling" [10]. Four sides of each specimen were coated with an epoxy resin and cured for one week at 20 °C, while the upper surface and the correspondent back side were not covered to allow a free circulation of water vapour. Three replicas for each mixture were put in a Global UV test GUT 200 chamber (WEISS Technik) and subjected to six hours cycles performed alternating: 5 hours and 45 minutes of continuous irradiation of the samples with UV light (290 nm – 400 nm, radiant energy Ee = 41 W/m^2); 15 minutes of dousing with water at 15 °C (conductance < 25µs/cm, dousing rate 40 $Lmin^{-1}m^{-2}$ corresponding to ~960ml of water/sample every cycle). 140 cycles were performed for a total of 35 days of exposure. Photographic documentation of the specimens was performed before, during and after the ageing test.

Table 1. Composition and starting properties of water repellent mixtures

Sample denotation	Binder type	Water-repellent 1% by mass	Real density (g/cm^3)	Bulk density (g/cm^3)	Total open porosity (vol.-%)	Modal pore radius (µm)*	σ_{max} (MPa)
CM	CEM II /B-L b/a 1:4 w/b 0.9	-	2.73	1.68	29.8	0.1; 1	11.70
CM750		Sitren p750		1.66	28.9	0.1; 1	8.25
CM730		Sitren p730		1.81	27.4	1	15.76
CMcast		Ca Stearate		1.78	28.7	0.02; 0.2	14.56
CMznst		Zn stearate		1.82	26.2	0.02; 0.1	9.27
NM	NHL3.5 b/a 1:5.1 w/b 0.5	-	2.74	1.53	47.3	1	1.32
NM750		Sitren p750		1.18	50	2	0.89
NM730		Sitren p730		1.32	55.2	0.3; 2	0.74
NMcast		Ca Stearate		1.35	52.5	5	0.62
NMznst		Zn stearate		1.35	41.4	0.5	0.62
PM	Lime + pozzolan b/a 1:7 w/b 1.3	-	2.60	1.77	25.0	0.1; 9	2.00
PM750		Sitren p750		1.44	36.0	0.1; 9	1.07
PM730		Sitren p730		1.69	26.9	0.2; 9	1.20
PMcast		Ca Stearate		1.73	24.9	0.1; 9	2.00
PMznst		Zn stearate		1.75	27.2	0.2; 9	0.26

b/a = binder-aggregate ratio by mass; w/b= water-binder ratio

*Maximum values of the multi modal pore size distribution

Analytical methods

Properties of water-repellent mortar specimens before the exposure

In order to evaluate the mortar structure and strength, before the exposure to the artificial weathering, the following properties were determined on 3 to 6 specimens according to the referred methods:

- Bulk density, calculated on dried prismatic specimens considering the ratio between their masses and their apparent volumes; material density (specific gravity) measured with a helium pycnometer on ground samples (powder diameter < 63 µm);
- Pore size distribution of the mortars by Hg-intrusion (MIP) [11];
- Compressive strength, according to UNI EN 12390-3:2009 [12] with a Zwick/Roell Z010 press (pre-load =20 N; loading rate= 50 N/s).

Evaluation of the exposure effects

In order to evaluate the effects of the weathering on surface appearance and the behavior of the specimens with respect to liquid water, before and after the artificial weathering the below listed properties were measured according to the following methods:

- surface colour, expressed as CIE L*a*b* coordinates (hue a* and b*, Lightness L*) and the total colour difference (ΔE*), measured with a CM2600d Konika Minolta portable spectrophotometer in the 360-740 nm range with a D65 illuminant, the measure spot size was 11 mm in diameter [13].
- capillary water absorption at (23 ± 2) °C [14];
- wettability of the mortar surfaces, determined by contact angle measurements of water drops [15].

In order to identify the presence of new hydrate phases or the possible degradation of the water repellent agents, the study included the monitoring of the surfaces via FT-IR spectroscopy, before and after the exposure. KBr pellets with samples of crushed mortar were analyzed with a Nicolet Nexus 670/870 spectrometer in the 4000-400 cm^{-1} region at 4 cm^{-1} of resolution [6].

RESULTS AND DISCUSSION

Pore structure and mechanical properties of mortars before weathering

The determination of bulk density, total open porosity, the modal pore radius and the compressive strength of the mixtures (Table 1) allowed to evaluate the structure and the strength of the mortars before the artificial weathering and to consider the influence of the admixtures on the systems, this information being necessary to understand the behavior during the weathering test. The modal pore radius data listed in Table 1 refers to the pore size distribution, indicating the center of the peak/s of the mono/multi-modal distribution. Averaged values of the real density were calculated for each kind of mortar, as negligible differences were observed between mortars admixed with different water-repellents.

The bulk densities (1.3 to 1.5 for NMs; 1.4 to 1.7 for PMs; 1.68 to 1.8 for CMs) showed differences between the mixtures following the binder-aggregates ratio and, to a small extent, to the admixtures used. The total open porosity shows an inverse relationship to the bulk density, increasing whenever the bulk density decrease indicating that the closed porosity remains constant for the different mortars.

The determination of the pore size distribution next to the total open porosity could provide further information on the weathering behavior: the presence of small pores, in fact, is associated to enhanced capillary absorption and lower weathering resistance [4, 5].

Limestone cement mortars mostly shows bimodal distribution except for CM730; natural hydraulic lime mortars mostly show a mono-modal distribution except for NM730 which has a bi-modal distribution; the pozzolana lime mortars showed a bimodal distribution centred at around 0.1 μm and 9 μm which remain quite similar in the different mixtures.

The pore size distribution of mortars with different binders did not show common trends depending on the presence of calcium stearates or Sitren P730. In all cases, Sitren P750 caused an increase of the porosity, while the pore size distributions remained similar to the reference mortars. In presence of zinc stearates, the distributions tended to shift to lower pore radius.

The strength of the mortars was primarily influenced by the binder used and secondarily by the water-repellent admixtures which mostly caused a slight decrease in the strength values. In most cases this could be linked to the increase in porosity. The presence of Zinc stearates in pozzolan-lime specimens caused a dramatic loss of the compressive strength, even if the bulk density was similar to the reference mortar PM, and might be attributed to a delayed hydration rate caused by the presence of the admixture.

Effects of artificial weathering

Appearance and colour changes

In the artificial weathering test the total UV radiant exposure was calculated to be approx. 130 MJ/m², the total amount of rain applied was approx. 135 litres/specimen corresponding to 84.000 L/m^2, with 140 temperature cycles (15 °C / 50 °C). Although it is not possible to establish a direct correlation between the laboratory tests and natural out-door weathering tests, it is possible to assume a reciprocity of the test to natural outdoor ageing considering that the average radiant exposure in Veneto -North Italy- is estimated to approx. 150 MJ/m^2 per year and 1060 mm of rain (1060 L/m^2) has fallen on Veneto in 2012 [16].

Figure 1 shows the surfaces of the more interesting specimens before and after the artificial weathering. The specimens of Portland limestone cement did not undergo significant deterioration processes, while the natural hydraulic lime mortars and the pozzolan-lime mortars were affected.

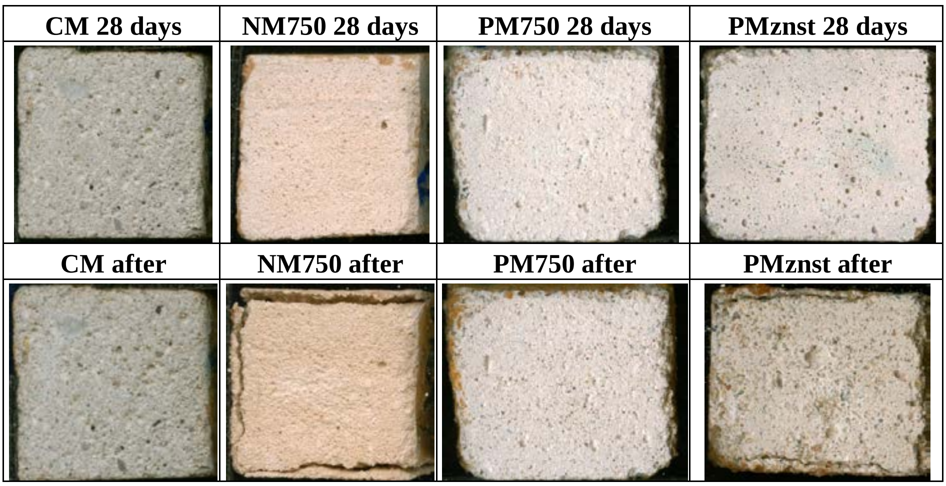


Figure 1**.** Pictures of some mortar mixtures before and after the weathering

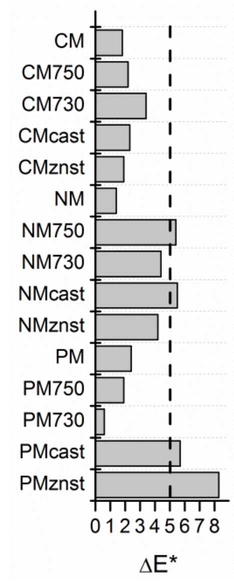
The mortars without water repellents CM, NM, PM showed slight surface powdering, small cracks at the edges and a preferential leaching of the binder followed by loss of aggregates. NM, PM showed also detachments of the epoxy layer due to differences in shrinkage and thermal dilation of the epoxy layer and the mortars as humidity and thermal changes occurred.

Two different types of ageing behavior of the mortars were observed. Those containing calcium stearates or zinc stearates behaved like the specimens without admixtures: cracks formed by the first 32-56 cycles and homogeneous crumbling of the exposed surfaces. The specimens with siloxane admixtures showed better durability: less crumbling and powdering was observed.

Moderate colour variations were evident after the test (Table 2), in particular for NM specimens and PMcast, PMznst where a change of ΔE=8.3 was attained. The colour variations were mainly due to the preferential leaching of the bright binder and the uncovering of darker aggregates. This caused a colour change with the increment of the chromaticity coordinates a* (reddish) and b*(yellowish) and the decrease of the Lightness L*.

Table 2**.** Colorimetric data of mortar mixtures before and after the exposures in different conditions. Lightness L* and chromaticity a*(red-green), b* (blue-yellow); average of nine measurements.

Mixture denotation	**28 days hardened mortars**			**after the exposure to UV-light and rain**			**Total colour variation**
	L*	a*	b*	L*	a*	b*	ΔE*
CM	72.8	0.6	7.2	71.0	0.3	7.2	1.8
CM750	67.4	0.5	6.7	67.6	0.7	8.9	2.2
CM730	70.0	0.6	6.8	66.9	0.6	8.0	3.4
CMcast	71.2	0.4	6.6	73.5	0.4	6.8	2.3
CMznst	72.5	0.5	7.5	70.9	0.7	8.5	1.9
NM	83.9	3.0	11.9	83.9	2.5	10.6	1.4
NM750	84.7	2.8	10.0	80.1	3.4	12.8	5.4
NM730	86.9	2.3	8.5	83.7	2.9	11.5	4.4
NMcast	85.7	2.5	2.5	81.8	3.3	12.9	5.5
NMznst	84.1	2.9	2.9	80.0	3.0	11.7	4.2
PM	82.6	1.2	5.7	81.4	1.9	7.7	2.4
PM750	84.6	1.0	5.0	83.7	1.6	6.5	1.9
PM730	86.6	0.6	5.1	86.3	1.1	5.3	0.6
PMcast	84.3	1.0	5.1	79.4	1.9	7.9	5.7
PMznst	84.9	1.0	5.3	79.3	2.0	8.0	8.3



Behavior with respect to liquid water

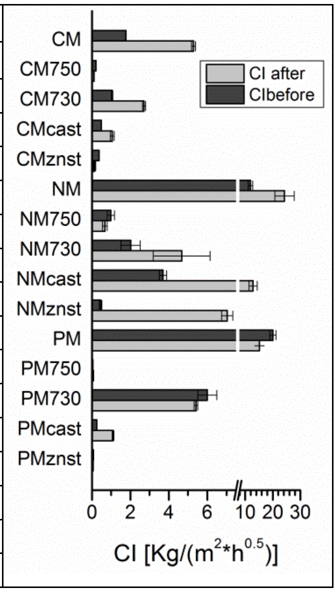
The aim of adding water repellent admixtures to mortars is to obtain increased durability by minimizing water uptake, therefore, the evaluation of this behavior was carried out. Table 3 presents the capillary water absorption coefficients and the contact angles measured before and after artificial weathering.

Before artificial weathering, the capillary absorption was significantly reduced by the presence of water repellent admixtures: the product Sitren P750 seemed the most effective in reducing water uptake and diminishing surface wettability. Also the stearates diminished the capillary absorption but the surfaces remained wettable (contact angles lower than 90°).

After artificial weathering consistent variations of the capillary absorption coefficient were observed. The significant increase of the water absorption observed for CM, CM730, CMcast, NM750, PMCast, might be related to an increased surface porosity; to the formation of cracks and to the erosion/wash-out of the water-repellents together with the binder. On the other side, the mortar mixtures CM750, CMznst, NM, NM730, NMcast, NMznst, PM, PM730 showed a decrease of the capillary water absorption coefficient. Probably the UV radiations, the corresponding high temperatures, and the high relative humidity (due to the artificial rain), allowed the binder matrix to further hydrate on the external surfaces becoming more compact, therefore reducing the external open porosity, the capillary water absorption and also the wash-out of the water-repellent admixtures from the surfaces. However, although the capillary water absorption decreased, the surfaces after the test were completely wettable. This could be attributed to the deterioration of the water–repellent admixtures on the surface from UV exposure. This is in agreement with field observations on natural stone treated with silicone resin [17] and laboratory studies on blended cements impregnated with silanes [7, 18].

Table 3. Behavior in presence of liquid water before and after the two exposures. CI= Capillary water absorption coefficient obtained by the average of three samples, α= contact angle.

Mix name	**hardened 28 days**		**after artificial weathering**	
	CI (kg/($m^2 \cdot h^{0.5}$))	**α°**	**CI** (kg/($m^2 \cdot h^{0.5}$))	**α°**
CM	1.77±0.02	*	5.29±0.10	*
CM750	0.21±0.01	**98±7**	0.11±0.01	*
CM730	1.05±0.04	61±6	2.71±0.08	*
CMcast	0.48±0.01	89±5	1.05±0.10	*
CMznst	0.37±0.02	80±4	0.13±0.06	*
NM	11.9±0.8	*	24.2±3.5	*
NM750	0.98±0.19	120±8	0.67±0.12	*
NM730	2.01±0.51	80±3	4.67±1.48	*
NMcast	3.69±0.19	*	12.84±1.45	*
NMznst	0.45±0.06	80±3	7.04±0.29	*
PM	20.0±1.1	*	15.10±0.01	*
PM750	0.05±0.01	130±6	0.07±0.01	*
PM730	6.0±0.5	*	5.41±0.09	*
PMcast	0.25±0.02	*	1.10±0.04	*
PMznst	0.07±0.01	118±14	0.06±0.01	*



* = completely wettable; nd = not determined because the specimens were completely disintegrated.

FTIR Assessment of mortar surfaces

FT-IR analysis of Portland limestone cement mortars (Fig. 2) before the weathering showed the peaks of silicates and carbonates present in the starting materials (IR absorptions at 900-1000 cm^{-1} and at 1436 cm^{-1} respectively); the peaks due to hydration of the binder such as calcium hydroxide (3640 cm^{-1}) and calcium silicate hydrate phases (C-S-H 950 cm^{-1}) and the peaks at 2920-2850 cm^{-1} due to aliphatic groups of calcium and zinc stearates visible in CMcast and CMznst. After artificial weathering, the FT-IR spectra of CMs mortars the calcium hydroxide absorptions were absent and the Si-O-Si stretching peak at 950 cm^{-1} of

C-S-H became visible in all the spectra, except for CMznst; this indicates a complete carbonation and a further hydration of the exposed surfaces during the ageing due to the high temperatures and moisture conditions. The peaks related to the water repellents were partially concealed by the other absorptions, but the complete absence of the aliphatic stretching at 2920-2850 cm^{-1} of CMcast and CMznst suggests the absence of any stearates on the mortar surfaces by the end of the exposure.

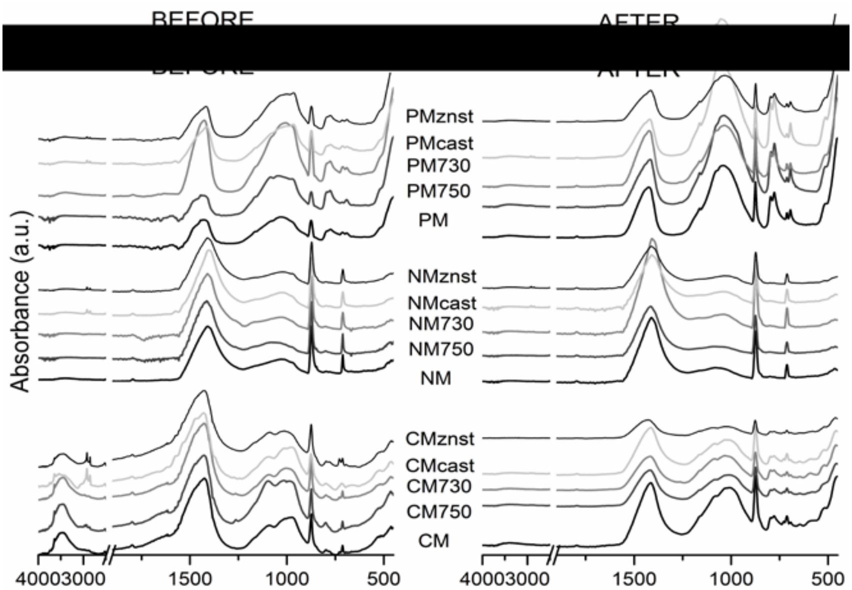


Figure 2**.** FT-IR spectra of the mortar surfaces before and after the artificial weathering

Spectra with similar absorption were registered for the natural hydraulic lime mortars, but in this case a higher presence of calcium carbonates (1436 cm^{-1}, 875 cm^{-1}) and a lower presence of silicates (900-1100 cm^{-1}) was detected. After the artificial weathering complete carbonation had taken place. The aliphatic absorptions at 2920-2850 cm^{-1} of calcium and zinc stearates were clearly detected indicating that the total wash-out of the water repellent did not occur.

The FT-IR spectra of the pozzolan-lime mortars before the weathering revealed the presence of alumino-silicates (Si-O-Si stretching at 1098-1009 cm^{-1}) due to the pozzolan and the formation of calcium silicate hydrate phases C-S-H (around 970 cm^{-1}). This second peak was observed in particular in the FT-IR spectra of PM750, PMcast, indicating a faster hydration. The peak was completely absent in PMznst denoting a slow hydration rate. Presence of calcium carbonate and aliphatic –CH stretching at 2920-2850 cm^{-1} due to the stearates in PMznst and PMcast were also visible. After weathering, the shift of the Si-O-Si stretching absorption to around 1000 cm^{-1} (related to the further production of C-S-H) was observed in every sample, indicating further hydration. No calcium hydroxide was observed at the end of the exposure in the external layer up to 0.5 cm depth.

CONCLUSIONS

The durability assessment of the mortars with and without hydrophobic admixtures exposed to UV-light, water, and thermal shock was the central step of this study to evaluate the performance of the admixtures. Based on the results obtained, the most damaging effects of the ageing test could be attributed to the mechanical stress resulting from high and low temperature cycling that induced crack formation while surface water repellency was reduced by UV-light exposure.

The resistance to artificial weathering depended both on the water-uptake (i.e., on the water-repellent effectiveness) and on the mechanical properties (i.e., on the binder used and on their interaction with the admixtures). Low capillary water absorption together with high strength resulted in a higher resistance, however, specimens such as PM750, PM730 and NM730 with low water uptake and low mechanical strength also showed good durability. Portland limestone cement mortars with and without water-repellent admixtures showed high weathering resistance, due to their high mechanical strength.

It was found that the durability of mortars can be ensured by the use of siloxanes, and to some degree, by metal soaps. However, the reduction of the capillary water absorption due to the use of the admixtures cannot always guarantee better durability by itself, because the use of admixtures influences other properties (mechanical strength, porosity). This was the case for PMcast, PMznst in comparison to PM, or for NM750, NMcast, NMznst in comparison to NM. In particular, the use of zinc stearates influenced the hydration reactions and the mechanical properties affecting the durability.

The effectiveness of the siloxanes admixtures can vary due to the product formulation (e.g., the type and percentage of siloxane used to cover carrier grains), and previous studies of the mechanical-physical behavior of water-repellent mortars admixed with siloxanes supported on silica powder have found an enhanced durability was observed [1- 3, 5]. The present study contributes to this topic, testing the physical properties of other types of water-repellent mortars and continues to evaluate the chemical interactions between admixtures and mortars by means of FT-IR analysis [6].

The results led to the conclusion that the choice of a suitable product can fall on a less effective product, in terms of water uptake reduction, but that demonstrates longer durability. A systematic investigation of the behavior of admixed mortars in different environmental situation is therefore strongly advisable.

Acknowledgments

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