The Baroque architecture of Scicli (south-eastern Sicily): characterization of degradation materials and testing of protective products

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Abstract

Scicli and the other Baroque cities of the "Val di Noto" (Catania, Militello, Caltagirone, Palazzolo, Siracusa, Noto, Ragusa e Modica), were recently included in the World Heritage List. These cities were completely destroyed following the earthquake of 1693 and then were involved in an intense period of rebuilding and artistic flowering. In particular, Scicli was reconstructed with the almost exclusive use of a local calcarenite, which belongs to the Ragusa Formation.

Due to its nature, this carbonate rock undergoes to many alteration and degradation forms (chromatic alteration, alveolization, differential disaggregation, efflorescence, decohesion, exfoliation and detachment). Therefore, different products (beeswax, vegetable oils, natural and synthetic resins) were used in the past with the aim to preserve the monuments from decay.

In this study, through a diagnostic analysis, the degradation materials occurring in the churches of St. Matteo, St. Michele and Carmine in the city of Scicli, as well as residues of treatments carried out in the past, have been identified.

In addition, three different types of protective products were tested in laboratory, with the aim of assessing their protective effectiveness in terms of hydrorepellence and response to accelerated aging and salt crystallization tests.

Laboratory tests showed that, among the tested products, the Polisiloxane can be regarded as the most suitable for this type of substrate.

Key words: calcarenite; south-eastern Sicily; degradation; protective products; accelerated aging tests; salt crystallization tests.

Introduction

Many stone monuments located outdoors are presently exposed to the risk of being irreparably lost due to the degrading effects of natural weathering and air pollution. Where stone is severely weakened by decay, consolidation may

be necessary to restore its strength. However, in some cases the treatment of stone materials in the conservation of Cultural Heritage leads to either insufficient protection or to the intensification of stone deterioration. This is particularly the case when treatment is carried out without adequate knowledge of the properties of the polymer/stone system and, moreover, without a satisfactory optimization of the molecular structures for protection purposes (Ashurst and Dimes, 1998; Rossi-Manaresi, 1975).

Various classes of synthetic organic coatings, e.g. acrylic and siloxane polymers, perfluoroethers fluorinated polyolefins, tetraethoxysilane (Alessandrini et al., 2000; Appolonia et al., 1995), have been tested in time as protective products, with the aim of improving the physical properties of stone materials. However, many conservation materials used in the past for specific interventions proved to be inappropriate, lacking chemical relevance to the substrate and thus intensifying deterioration of the stone after their application (Moropoulou et al., 2003).

In such a context, an important case study is represented by the Baroque cities of the "Val di Noto" area, in south-eastern Sicily (Figure 1), which after the severe earthquake of 1693 were reconstructed with the almost exclusive use of locally outcropping carbonatic lithotypes. In the last years, several studies have been carried out on the decay of monuments of these Sicilian Baroque cities (Barone et al., 2008; La Russa et al., 2010 and references therein) mainly focusing on the individuation of the protective products suitable for their conservation. Here we focus on the city of Scicli (Figure 1), where, despite conservation measures carried out in the past, many of the monumental buildings and churches, built in a local calcarenite (commonly known as "Scicli calcarenite"), are still undergoing severe degradation. The commonest degradation forms observed in the three investigated churches (Carmine, St. Matteo and St. Michele; Figure 2), as well as in all the most important monuments of the city, include: chromatic alteration, alveolization, differential disaggregation, efflorescence, decohesion, exfoliation and detachment (Figure 3). The main cause of degradation is salt crystallization, which produces microstructural modifications within the rock and, at the same time, generates matrix dissolution with consequent increase in porosity and disaggregation of the stone.

Information regarding restoration works carried out in the past in these three churches are scarce. The historical documents preserved at the Superintendence of Cultural Heritage of Ragusa
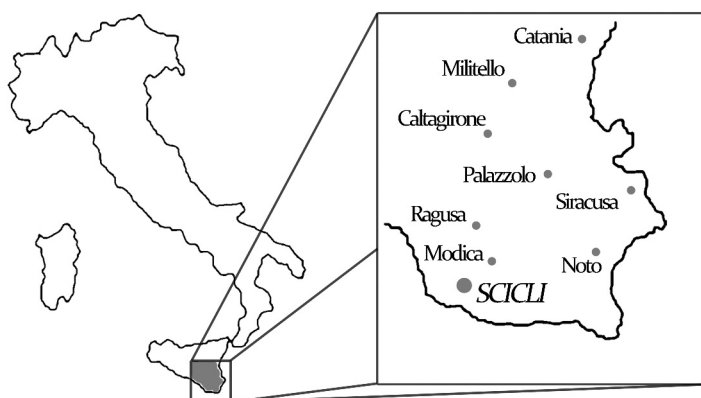

Figure 1. Scicli and the other Baroque towns of the "Val di Noto" area (south-eastern Sicily).

Figure 2. Façades of the three investigated churches: a) Carmine; b) St. Matteo; c) St. Michele.

refer to previous interventions, but only indicating the periods in which these restorations were made (1990 in the church of Carmine, 1980-90 in St. Matteo and 2008 in St. Michele), without any specific indication of the products used for treatments.

Therefore, through a diagnostic analysis of these three churches, this work aims at individuating the principal degradation forms and the protective products eventually used in past. In addition, three different types of protective products are here tested on calcarenite samples taken from an historical quarry nearby, in order to highlight the interactions between protective products and substrate, particularly after accelerated aging by UV and salt crystallization.
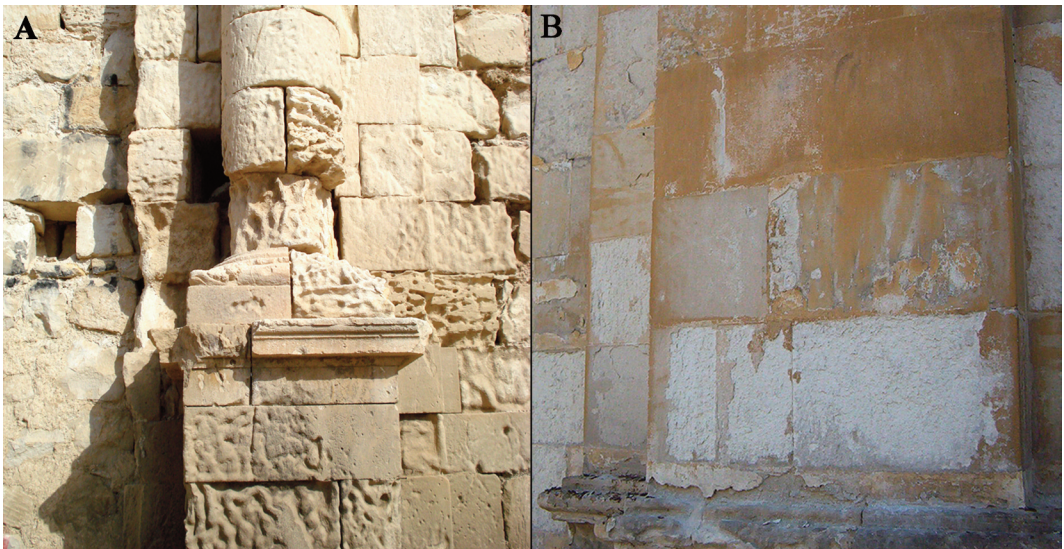

Figure 3. Two examples of the commonest degradation forms observed in most of the monuments of the city: a) alveolization (church of St. Matteo); b) chromatic alteration and exfoliation (church of Carmine).

Historic and geological setting

Scicli is one of the most significant examples of the Sicilian Baroque, which belongs to the "Val di Noto", an area in south-eastern Sicily which recently became part of UNESCO's World Heritage List. The importance of Scicli (as well as of the other Baroque centers in this area) is partly due to the severe earthquake of 1693 which entirely destroyed the previous city, then completely rebuilt in the style of Baroque architecture.

The churches investigated in this work include: a) the Church of Carmine, built in the first half of the XVIII century, has one of the most beautiful façades of the entire Baroque architecture in eastern Sicily; b) the Church of St. Matteo, representing the symbol of Scicli, dates back at least to the XI century. Strongly and irreparably damaged after the earthquake of 1693, it was rebuilt since 1703 for an entire century, even if the main façade was never completed; c) the Church of St. Michele Arcangelo, probably built between 1740 and 1750, was completed only in 1859 (Cataudella, 1988).

From a geological viewpoint, the calcarenite of Scicli is associated to the Ragusa Formation (Upper Oligocene-Miocene). This latter consists of two members (Di Grande and Raimondo, 1982): a) the lower Leonardo Member (Upper Oligocene), formed of alternating calcareous and marly layers; b) the upper Irminio Member (Lower Miocene), consisting of three different levels: i) a calcarenitic basal level; ii) an intermediate marly-calcarenitic alternance; c) an upper marly-calcarenitic alternance (Di Grande et al., 1977).

The calcarenite of the Irminio Member, which was abundantly extracted from the many quarries occurring nearby, was extensively used to construct the post-earthquake cities of Val di Noto (Rodolico, 1965).

Materials

Calcarenite samples from monuments

Examined materials consist of 14 oriented samples of superficial layers of calcarenite stone, taken from the principal façades of the three investigated churches in Scicli (Table 1). Stainless steel tools and surgical lancets were used, and the main criteria for sampling included good state of aggregation, available quantities, and representativeness. The samples taken from the above mentioned churches are mostly orange in color and appear macroscopically intact and durable, except for a few which are very friable probably due to salt crystallization.

Scicli calcarenite from quarry

A total of 20 calcarenite specimens, belonging to the Ragusa Formation (the basal level of the Irminio Member), were also taken from one of the historic quarries located near the ancient city of Scicli. Samples were collected taking into account their homogeneity and the lack of fractures and/or degradation forms.

Macroscopically, all the samples appear to be homogeneously fine-grained and whitish in color.

From a microscopic viewpoint, the Scicli calcarenite displays a homogeneous and grain-supported texture. The abundance of allochemical components is around 40%, consisting of fossils (90% - planktonic and benthic foraminifera, bryozoa fragments and echinoids) and of peloids (10%). The cement (abundance 20%) is of the syntaxial and sparry types, while the matrix (40%) is micritic. The porosity is high (around 35-40%) and is prevalently primary. Samples can be classified as biomicrite (Folk, 1959) or packstone (Dunham, 1962).

Protective products

The organic products which were tested in the present study include: 1) Paraloid B72 (Rhom and Haas USA), an acrylic resin ethylmethacrylate methylacrylate copolymer; 2) Silo 111 (CTS), an

Table 1. Sampling sites and macroscopic description of the samples taken from the main facades of investigated monuments.

Investigated church	Samples	Sampling sites	Macroscopic description
Church of Carmine	SC1	At the base of the main facade	Orange patina not adhering to substrate
	SC2	At the left side of the portal	Orange patina not adhering to substrate
	SC3	At the left side of the portal	Orange patina not adhering to substrate
	SC4	At the right side of the portal	Orange patina not adhering to substrate
Church of St. Matteo	SC5	At the right portal	Orange patina well adhering to substrate
	SC6	At the right portal	Orange patina well adhering to substrate
	SC7	At the right side of the main portal	Pale yellow patina well adhering to substrate
	SC8	At the left portal	Brownish patina well adhering to substrate
	SC9	At the left portal	Pale yellow patina well adhering to substrate
	SC10	At the base of the column the main portal	Pale yellow patina well adhering to of substrate
Church of St. Michele	SC11	At the right side of the portal	Pale yellow patina not adhering to substrate
	SC12	At the left side of the portal	Orange patina not adhering to substrate
	SC13	At the left side of the portal	Pale yellow patina not adhering to substrate
	SC14	At the left side of the portal	Pale yellow patina well adhering to substrate

organosiloxane oligomer; 3) PVA K40 (CTS), a vinyl acetate homopolymer.

These protective products were chosen for their hydro-repellent and consolidating properties, and after an accurate diagnostic analysis of the Scicli building stone.

Analytical methods

FT-IR spectroscopy analysis was performed for the mineralogical and organic characterization of the samples taken out from the façade of the three churches, with the aim to individuate secondary phases due to degradation and the protective products eventually used in the past. For this reason, samples were subjected to organic extraction using acetone. The extracted phases were allowed to dry and then analyzed. The equipment used was a NICOLET 380 with a Smart Orbit accessory, used in the following arrangement: a K-Br beamsplitter, a HP-DTGS-KBr detector and an Ever-Glo lamp used as source. Infrared spectra were recorded in attenuated total reflectance mode, in the range of 500-4000 cm^{-1} at a resolution of 4 cm^{-1}.

Experimental tests, finalized to verify the efficacy of protective treatments on the Scicli stone, have been carried out on the quarry samples. The detailed procedure of sample preparation and testing is described below.

Sample preparation and testing
Experiments were performed on squared blocks (5 x 5 x 5 cm) stored in desiccators at 25°C for at least 24 h before application of the coating, as required by the UNI 10859 norms (2000). The

protective products were brushed on one face of the cube (two samples have been used for each applied amount).

The most suitable amounts of protective products were first roughly estimated according to porosimetric data, and then tested through the capability of the samples to absorb the products. The exact amounts of applied product (QP%) (NORMAL 20/85, 1996), reported in Table 2, were calculated by weighing the samples before and after application. In particular, after the application of protective products, the samples were located in an oven until they reached a constant weight. QP% was calculated using the following relation: QP%=$(M_2-M_1)/M_1*100$, where M_1 and M_2 indicate the constant weights of samples before and after the treatment, respectively.

All treated samples underwent laboratory

Table 2. List of tested protective products and relative amounts applied to surface of samples.

Protective product	Amount applied	Samples	QP %
SILO 111	20 gr/m^2	SIL1A	0.11
		SIL1B	0.13
	10 gr/m^2	SIL2A	0.07
		SIL2B	0.09
	40 gr/m^2	SIL3A	0.18
		SIL3B	0.18
PARALOID B72	20 gr/m^2	PAR1A	0.01
		PAR1B	0.03
	30 gr/m^2	PAR2A	0.04
		PAR2B	0.03
	40 gr/m^2	PAR3A	0.04
		PAR3B	0.04
PVA K40	20 gr/m^2	VIN1A	0.01
		VIN1B	0.02
	30 gr/m^2	VIN2A	0.04
		VIN2B	0.03
	40 gr/m^2	VIN3A	0.06
		VIN3B	0.08

procedures to determine interactions between substrate and applied products. Specifically, performed tests include:

i) Capillary water absorption (UNI 10859, 2000), to obtain capillary absorption curves and the relative absorption index (IC_{rel}). The latter is particularly indicative of the aptitude of the protective products since their hydrophobic effect is inversely related to the IC_{rel} value. This parameter is defined as the ratio between the area under the capillary absorption curve of treated (Q_t) and untreated (Q_u) samples, calculated from the beginning (t_0) to the end (t_f) of the test (UNI 10859, 2000; Peruzzi et al., 2003):

$$IC_{rel} = \frac{\int_{t0}^{tf} f(Qt)dt}{\int_{t0}^{tf} f(Qu)dt}$$

In addition, the capillary protection ratio (Ec%), which represents the amount of capillary water absorbed by a treated sample after a definite time t, has been also calculated. Ec% is defined as the percentage ratio between the difference of capillary water absorbed by a sample at the time t (in our case after twenty minutes from the beginning of the test), before (A_1) and after (A_2) treatment, and the quantity of water absorbed before treatment (A_1): Ec% = $(A_1-A_2/A_1)*100$.

For capillary water absorption test, dried samples were weighed and separately placed in vessels containing a pile of filter papers immersed in water up to half of their depth, with one face of the sample lying on the paper. Absorption occurred only through the base, by vertical suction. The containing vessels were sealed and kept at a constant temperature of 20°C. At regular intervals, the samples were extracted and weighed, after sponging with a damp cloth to eliminate excess water.

ii) Accelerated aging tests, performed with light emitted by a 300-W OSRAM Ultravitalux light with a UV-A component. The procedure recommended by UNI 10925 norm (2001), with

some modifications as suggested by Barone et al. (2008), has been followed. Testing was carried out in two steps, at 340 and 580 hours respectively, in order to evaluate the stability of the hydrophobic property of the protective film.

iii) Accelerated aging tests by salt crystallization (UNI EN 12370, 2001), in order to assess the resistance of the protective products to salts. Tests were carried out by continuous partial immersion, as proposed by Benavente et al. (2001). In particular, samples underwent 15 2-hour cycles at 20°C in an aqueous solution of decahydrate sodium sulphate ($Na_2SO_4 \cdot 10H_2O$) at 14% v/v and subsequent heating for 16 h at 105°C.

iv) Mercury intrusion porosimetry (MIP) measurements carried out on an Auto Pore IV Micromeritics porosimeter, to evaluate possible modifications induced by the protective treatment on the sample porosity. Sample size was 1cm from the treated surface for all specimens.

v) Colorimetric tests on a CM-2600d/CM2500d Konica Minolta spectrophotometer, to assess chromatic variations induced by application of protective products and aging of samples (NORMAL 20/85, 1996; Vigliano, 2002). Five measurements, in the four corners and at the centre, have been performed only in the face interested by the treatment.

Results

FT-IR spectroscopy analysis of samples from monuments

The infrared spectroscopic analysis carried out on the samples from monuments has allowed the identification of different inorganic phases and organic products.

As expected, in all analyzed samples the stretching vibrations of calcium carbonate ($CaCO_3$), peaked at 1409, 705 and 611 cm^{-1}, were identified. In addition, in the stone materials from the church of Carmine the typical vibrational

bands of gypsum ($CaSO_4 \cdot 2H_2O$), centred at 1109, 669 and 596 cm^{-1}, were also indentified as well as the stretching and deformation vibrations of the O-H bond of water at 3525, 3492, 3401 cm^{-1} and at 1692 and 1627 cm^{-1}, respectively. The characteristic bands of whewellite, peaked at 1328 and 1615 cm^{-1}, and those of thenardite, centred at 1034 cm^{-1}, were also found.

The extracted phase of sample SC1 shows the stretching vibrations of polyvinyl acetate, centred at 944 cm^{-1} (C-O), l365 cm^{-1} (C-H), 1735cm^{-1} (C = O). The band at 708 cm^{-1} indicates the torsion of the C-H group (Derrick et al., 1999).

In the samples from the church of St. Matteo the bands of calcium oxalate (whewellite) and clay minerals were recognized, with peak at 1032 cm^{-1} (Si-O-Si bond), as well as the stretching and deformation vibrations of the O-H bond of water at 3525, 3492, 3401 cm^{-1} and at 1692 and 1627 cm^{-1}, respectively (La Russa et al., 2008).

Finally, in the samples taken from the church of St. Michele only clay minerals, together with calcite, were identified.

Representative FTIR spectra of the analyzed samples are shown in Figure 4.

Capillary water absorption test

The hydrophobic efficacy of the selected protective products was tested by means of capillary absorption tests. Analyses were performed on both untreated and freshly treated samples, as well as after accelerated aging by means of UV radiation. The absorption curves of the three types of samples are shown in Figure 5, where x and y axes represent the square root of time and the Q_i value, respectively. Q_i is the quantity of absorbed water per surface unit, expressed as: $Q_i = (m_t - m_0)/S$, where S is the area of the sample base, and m_t and m_0 are sample weights measured at times t and 0, respectively (UNI 10859, 2000).

The different behavior of the tested products is shown by the relative absorption index IC_{rel} and capillary protection ratio Ec% (Table 3).
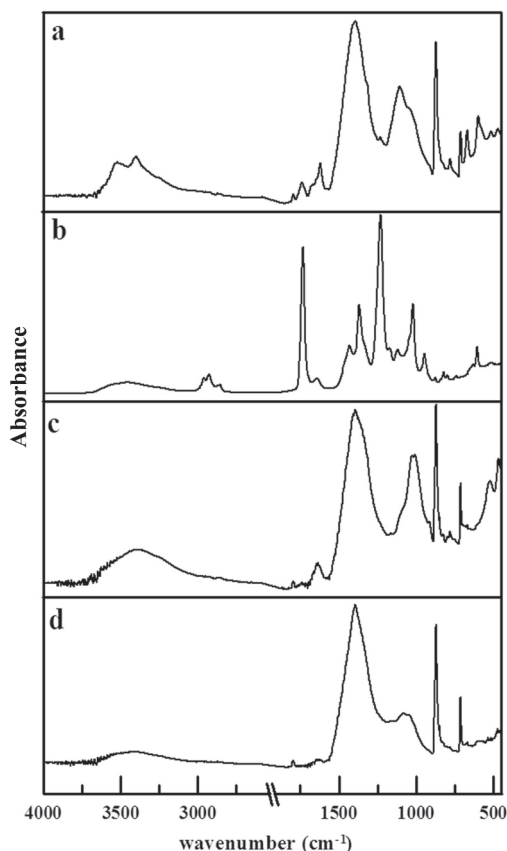
Figure 4. FTIR spectra of: a) sample SC1 from the church of Carmine; b) organic phase of sample SC1, extracted with acetone; c) sample SC5 from the church of St. Matteo; d) sample SC12 from the church of St. Michele.

Samples treated with SILO 111 show a considerable decrease of ICrel values from non-aged to aged specimens and an increase of Ec up to 98% starting from rather variable values (33%-58%-74%) of non-aged samples.

Specimens treated with PARALOID B72 display a slight increase of IC_{rel} values from non-aged to aged samples (more evident in PAR2), while Ec values generally decrease, even if a quite variable trend in the different samples is observed.

Lastly, samples treated with PVA K40 show a small increase of IC_{rel} values in aged specimens and a general decrease of Ec, except for VIN3.

Accelerated aging tests by salt crystallization

The salt crystallization test was performed on untreated, treated and aged samples in order to determine the effectiveness of each product to protect stone from salt degradation. The results are shown in Figure 6, where macroscopic variations during the most significant cycles and weight modifications at the end of the test are reported. As can be observed, the most important variations refer to the untreated samples which show a ΔM=56%. Samples treated with SIL show a different behaviour depending on the amount applied: the only samples which display a significant weight loss (ΔM=39%) are those treated with SIL 10 g/m^2, whereas those treated with SIL 20 gr/m^2 show a ΔM=22% and those with 40 g/m^2 do not suffer any weight modification. All the samples treated with PAR undergo considerable modifications: in particular, those with 20 and 30 g/m^2 lose 42% of their initial weight, those with 40 g/m^2 the 44%. Lastly, samples treated with VIN show the highest variations since their initial weight halves (ΔM is comprised between 49 and 53%).

Porosimetric analysis

The pore structure of Scicli calcarenite has been investigated by means of mercury intrusion porosimetry. This was performed on both untreated and treated samples (before UV and salt crystallization accelerated aging). The mercury intrusion porosimetry (MIP) value for untreated samples is comprised between 25 and 30%. MIP values for samples treated with SIL1, SIL2 and SIL3 are 29%, 27% and 32%, respectively. The samples treated with PAR display MIP values of 31% for PAR1, 26% for PAR2 and 31% for PAR3. Finally, samples treated with VIN show values of 28% (VIN1), 26% (VIN2) and 25% (VIN3).

Colorimetric test

Chromatic variations induced to the examined stone samples by the protective treatments have been evaluated through the determination of the ΔE parameter, which indicates the difference between each chromatic coordinate (L*, a* and b*) in both untreated and treated/aged samples. In particular, ΔE is defined by the following relation: $\Delta E=\sqrt{(\Delta L^*)^2+(\Delta a^*)^2+(\Delta b^*)^2}$, where L* is the lightness/darkness coordinate, a* the red/green coordinate (+a* indicating red and -a* green), and b* the yellow/blue coordinate (+b* indicating yellow and -b* blue), in the CIELAB notation. According to Italian guidelines (NORMAL 20/85, 1996) for the restoration of stone buildings, the ΔE value must be less than 5 (Vigliano, 2002). Measurements have been carried out before and after treatment as well after the two cycles of aging. The results are reported in Table 4. Color variations between

Table 3. Relative absorption index (ICrel) and capillary protection ratio (Ec) values for samples treated with the three protective products before and after accelerated aging. N.d.= not determined.

| Protective product	Samples	ICrel values			EC% values		
		Non-aged	Aged (340 h)	Aged (580 h)	Non-aged	Aged (340 h)	Aged (580 h)
SILO 111	SIL1A	0.80	0.36	0.41	63.51	97.88	96.98
	SIL1B	0.89	0.35	0.34	52.39	97.99	96.79
	Average	0.85	0.35	0.37	57.95	97.93	96.89
	SIL2A	0.67	0.48	0.55	76.15	97.93	96.32
	SIL2B	0.73	0.52	0.62	70.96	97.88	95.05
	Average	0.71	0.50	0.59	73.55	97.90	95.69
	SIL3A	0.85	0.56	0.52	42.25	95.90	96.98
	SIL3B	0.90	0.73	0.46	23.87	95.24	98.54
	Average	0.88	0.64	0.49	33.06	95.57	97.76
PARALOID B72	PAR1A	0.88	0.97	0.92	36.88	4.26	7.94
	PAR1B	1.07	1.14	1.07	1.36	6.65	8.24
	Average	0.98	1.06	1.00	19.12	5.55	8.09
	PAR2A	0.67	0.89	0.86	70.68	64.50	31.51
	PAR2B	0.79	1.06	0.99	44.85	7.89	0.25
	Average	0.74	0.97	0.93	57.76	36.20	15.88
	PAR3A	0.98	0.98	0.98	39.06	18.07	30.19
	PAR3B	0.81	0.83	0.84	72.47	48.81	79.26
	Average	0.90	0.91	0.91	55.76	33.44	54.72
PVA K40	VIN1A	0.88	1.03	0.97	35.20	7.05	8.60
	VIN1B	0.75	0.90	0.85	57.43	29.24	6.19
	Average	0.82	0.97	0.91	46.32	18.15	7.39
	VIN2A	0.91	1.01	0.94	39.76	8.13	n.d.
	VIN2B	0.91	1.00	0.93	39.19	19.39	n.d.
	Average	0.91	1.01	0.94	39.47	13.76	n.d.
	VIN3A	0.95	0.95	0.93	4.40	11.38	50.98
	VIN3B	0.83	0.85	0.84	24.06	18.83	62.52
	Average	0.89	0.90	0.89	14.23	15.10	56.75
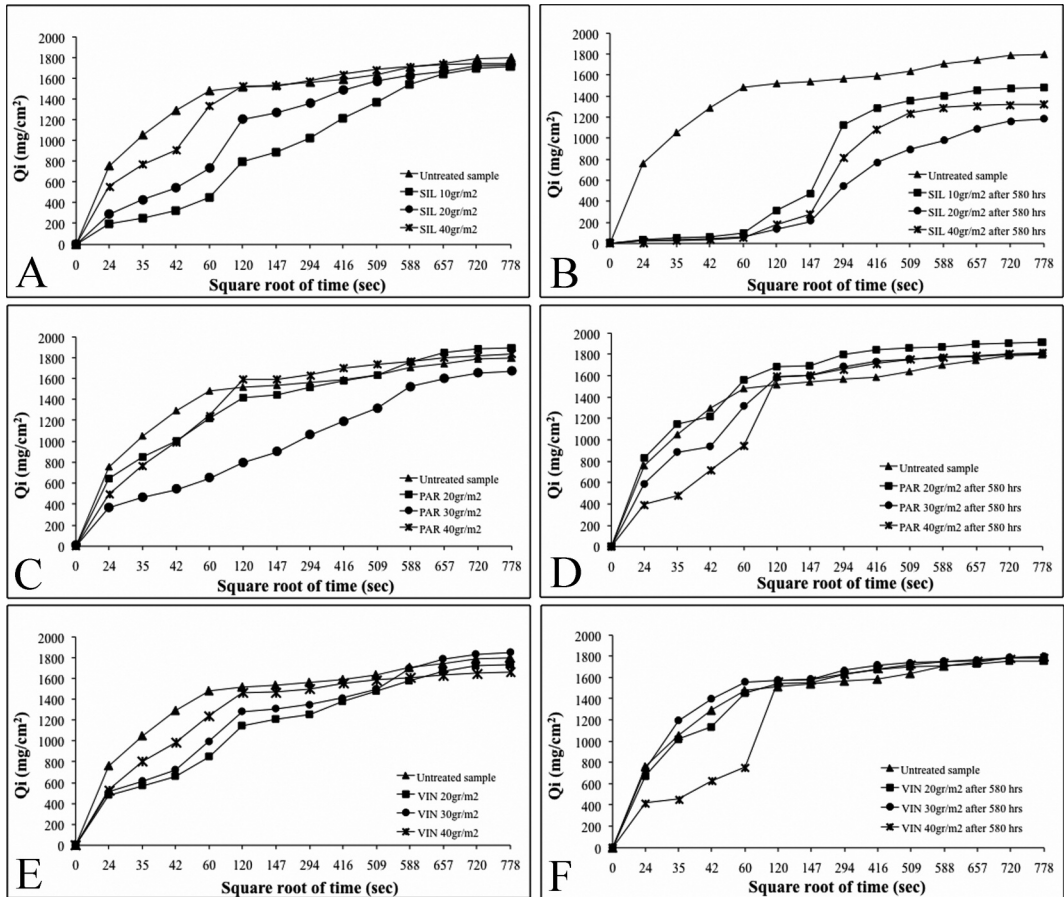
Figure 5. Water absorption curves relative to the three types of tested products. A and B refer to samples treated with SILO non-aged and aged, respectively; C and D refer to samples treated with PAR non-aged and aged, respectively; E and F refer to samples treated with VIN non-aged and aged, respectively.

untreated and treated samples are indicated with ΔE^*, those between treated and 340 hrs -aged samples with $\Delta E1^*$, and between treated and 580 hrs-aged samples with $\Delta E2^*$. The results can be also visualized in the histogram of Figure 7.

Discussion

FTIR data provided important information on the conservation state of the three investigated façades and on previous restoration works

performed on the same. In particular, regarding the church of Carmine, the presence of sulphates, such as gypsum and thenardite, has been recognised. Thenardite is considered to be one of the most aggressive salts for carbonatic rocks. As known in fact, at specific temperature and humidity ranges, a phase transition of thenardite to mirabilite occurs with a resulting volume increase in the order of 300% (Flatt, 2002). Hence, the necessity to select protective products which are able to inhibit the salt action. In
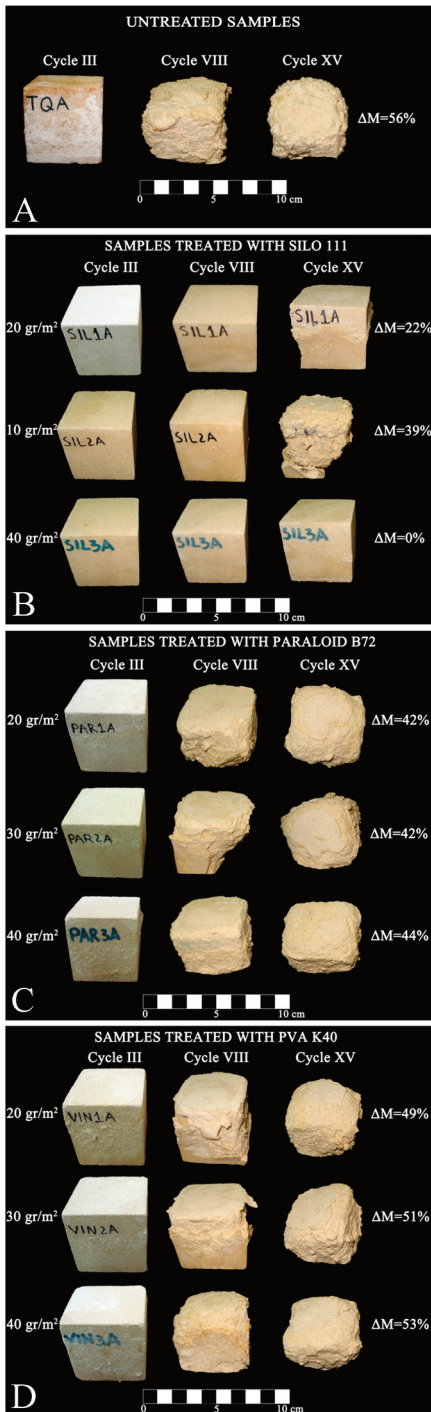
Table 4. ΔE values for samples treated with SIL, PAR and VIN.

Protective product	Samples	ΔE*	ΔE1*	ΔE2*
SILO 111	SIL1A	1.95	0.22	0.80
	SIL1B	1.93	2.88	4.78
	Average	1.94	1.55	2.79
	SIL2A	1.46	3.10	2.60
	SIL2B	1.55	3.05	0.38
	Average	1.51	3.08	1.49
	SIL3A	5.58	2.01	3.72
	SIL3B	3.37	2.53	3.82
	Average	4.48	2.27	3.80
PARALOID B72	PAR1A	3.95	0.37	0.79
	PAR1B	3.58	2.15	1.55
	Average	3.77	1.26	1.17
	PAR2A	5.33	1.59	2.50
	PAR2B	5.31	1.12	1.05
	Average	5.32	1.35	1.78
	PAR3A	6.49	0.96	1.52
	PAR3B	2.97	1.19	3.59
	Average	4.73	1.08	2.56
PVA K40	VIN1A	3.88	2.16	1.23
	VIN1B	3.15	2.97	1.61
	Average	3.52	2.56	1.42
	VIN2A	5.26	1.72	1.32
	VIN2B	5.24	1.51	1.24
	Average	5.25	1.61	1.28
	VIN3A	5.75	1.03	0.59
	VIN3B	4.76	0.49	0.60
	Average	5.26	0.76	0.60

addition, in the same samples, as well as in those from the church of St. Matteo, FTIR analysis allowed to individuate the occurrence of calcium oxalate. As known from literature (Del Monte, 2001; Krumbein, 2002), the origin of this phase can be related to metabolic processes in micro-flora (lichens or bacteria) on the stone surface or alternatively to past restoration works. In the case of church of Carmine, the presence of polyvinyl acetate points to a previous intervention, as documented by bibliographic sources.

Water capillary absorption tests showed that the same type of material interacts with the three tested products in different ways. In particular, samples treated with SILO 111 (Figure 5) display a different variation of hydrophobicity which is correlated with the different applied amounts and with the UV exposition period. All treatments with the three amounts give the stone a

UNTREATED SAMPLES

Cycle III   Cycle VIII   Cycle XV

TQA

$\Delta M=56\%$

0   5   10 cm

A

SAMPLES TREATED WITH SILO 111

Cycle III   Cycle VIII   Cycle XV

20 gr/m²   SIL1A   SIL1A   SIL1A $\Delta M=22\%$

10 gr/m²   SIL2A   SIL2A $\Delta M=39\%$

40 gr/m²   SIL3A   SIL3A   SIL3A $\Delta M=0\%$

B   0   5   10 cm

SAMPLES TREATED WITH PARALOID B72

Cycle III   Cycle VIII   Cycle XV

20 gr/m²   PAR1A $\Delta M=42\%$

30 gr/m²   PAR2A $\Delta M=42\%$

40 gr/m²   PAR3A $\Delta M=44\%$

C   0   5   10 cm

SAMPLES TREATED WITH PVA K40

Cycle III   Cycle VIII   Cycle XV

20 gr/m²   VIN1A $\Delta M=49\%$

30 gr/m²   VIN2A $\Delta M=51\%$

40 gr/m²   VIN3A $\Delta M=53\%$

D   0   5   10 cm

hydrorepellent property though the best result has been obtained with SIL 20 g/m², as demonstrated by the IC_{rel} values. As can be observed in Figure 5, samples treated with this amount show a considerable decrease of absorption between freshly treated samples and those 580-hrs aged. This result can be ascribed to the slow reticulation of the applied product which increases during the UV exposition. Concerning samples treated with SIL 10 and 40 g/m², results can be considered acceptable compared with the curve of untreated samples (Figure 5), even if IC_{rel} values are lower. Results obtained for samples treated with Paraloid B72 highlight that this resin is not appropriate for this type of carbonatic substrate. Particularly, specimens treated with PAR 20 and 40 g/m² do not show any hydrophobic property. The absorption curves of freshly treated and aged samples are in fact close to curves of the untreated ones. Lastly, regarding samples treated with PVA K40, the relative absorption curves (Figure 5) show that their hydrophobic property decreases during the UV exposition thus indicating a scarce stability over time. It's worth noting that the data obtained for the vynilic resin are in strong contradiction with respect to the last restoration works which have interested one of the investigated churches. As above discussed, in fact, evidences of this type of product have been found in the samples taken from the façade of church of Carmine.

The salt crystallization test also revealed different interactions between each protective product and the substrate. The results show that untreated samples start their chromatic alteration at the third cycle, while since from the fourth cycle sub-efflorescences appear and the capillary rise front is well visible. At the fifth, other

Figure 6. Degradation forms and weight modifications after salt crystallization aging test performed on samples treated with different amounts of protective products.
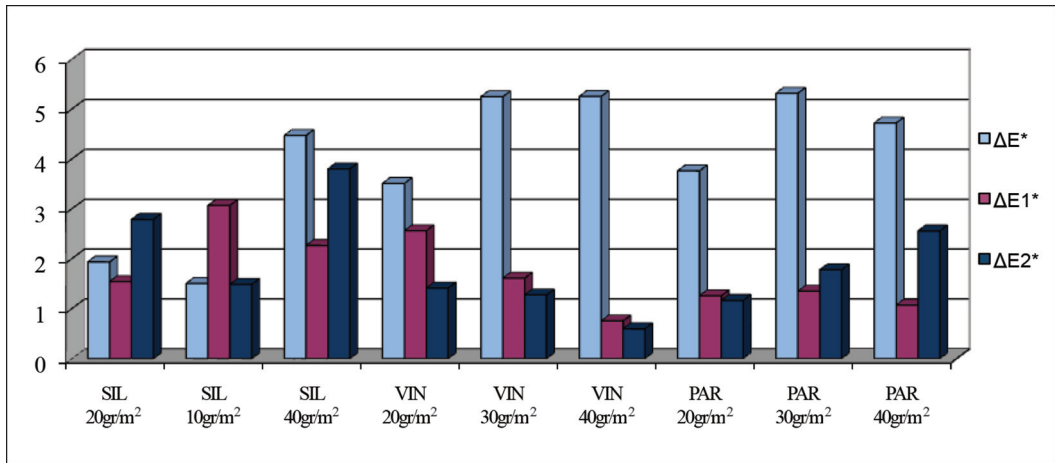
Figure 7. Histogram showing ΔE*, ΔE1*, ΔE2* values for samples treated with different amounts of SIL, PAR and VIN.

degradation forms, such as surface exfoliation and detachment, start developing. The weight loss at the fifteenth cycle is of 56%. Samples treated with SILO 111 show different behaviour depending on the applied amount. In particular, those with SIL 10g/m^2 highlight the capillary rise front at the fifth cycle, a slight chromatic alteration at the eighth and loss of edges together with marked exfoliation at the following cycles. The weight loss was of 39%. Regarding samples treated with SIL 20g/m^2, the capillary rise front is well visible only at the twelfth cycle, fissuration appears at the fourteenth and loss of edges at the fifteenth. The total weight loss was of 22%. Lastly, samples treated with 40 g/m^2 show a behaviour totally different from the previous ones since no degradation phenomenon has been observed until the end of the test. A slight weight increase (0.3%), probably due to small quantities of salts trapped inside, has been recorded. All samples treated with PAR show the same trend of degradation: at the second cycle a slight chromatic alteration occurs, at the fourth sub-efflorescence and surface swelling, while exfoliation and loss of edges during the following cycles. The weight loss was of 42%

for samples treated with 20 and 30 g/m^2, 44% for those with 40 g/m^2. All samples treated with VIN starting from the second cycle display a slight chromatic alteration and an initial development of sub-efflorescence, at the fifth the capillary rise front is visible, from the seventh considerable weight losses occur, which progressively intensify until the end of the test. Samples treated with VIN 20g/m^2 show a total weight loss of 49%, those with 30g/m^2 of 51% and those with 40g/m^2 of 53%.

The results of MIP analysis allowed to evaluate the modifications in the porous system induced by the application of protective products. In this respect, it has been observed that the total porosity of samples after treatment with the three tested materials does not decrease significantly with respect to untreated samples, so that they maintain one of their most important physical properties almost unchanged. It is a crucial aspect for good conservation performance since, as known, after the application of protective products the stone surface must not be sealed and pores must not be completely blocked, to allow the release of moisture which is often trapped inside

(Vacchiano et al., 2008). Pore obstruction could cause the appearance of further forms of degradation, such as swelling or detachment, which are due to poor interactions between substrate and protective product. The only modifications that can be appreciated for all three products (and for the different amounts applied) are relative to the distribution of porosimetric classes, particularly those comprised in the range 0.3 - 0.04 μm, i.e. mesopores.

Finally, as regards colour alteration of surface caused by protective treatment and accelerated aging, only PAR 30 g/m^2 and VIN 30 and 40 g/m^2 cause a variation which is visible to the naked eye, with a ΔE value higher than the acceptable limit (5.3, 5.2 and 5.3, respectively), according to Italian guidelines (NORMAL 20/85, 1996; Vigliano, 2002). All other treatments did not cause any significant variation, being ΔE values lower than 5.

Conclusions

This study remarks the importance of diagnostic analysis before any restoration intervention, since the interaction between any products (protective and/or consolidating) and the stone material, in terms of efficacy and reaction, is different according to minero-petrographic and physical properties of substrate.

In our case, the FT-IR spectroscopy analysis carried out on calcarenite samples from the Baroque churches of Carmine, St. Matteo and St. Michele in the Scicli city, has allowed the identification of degradation products (thenardite, calcium oxalate and gypsum) occurring on the investigated monuments as well as residues of protective treatments applied in the past in one of the three churches (Church of Carmine).

The experimental tests carried out on calcarenite samples taken from an historical quarry nearby, finalized to verify the efficacy of three different types of protective products, allowed to do the following considerations: a) the vinylic resin (PVA K40), showed the worst results, nevertheless it had been used in previous restoration work, as detected by IR analyses. Therefore, this product cannot be regarded as suitable for this type of substrate. b) The acrylic resin (Paraloid B72) did not give acceptable results in all tests; c) conversely, the organisiloxane oligomer (Silo111) resulted to be the most appropriate for this calcarenitic material in terms of water repellency and response to salt crystallization tests.

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