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Innovative Evaluation of the Performances of Water-Repellent Treatments by IR Thermography

A. Sansonetti[1], M. Casati [1], E. Rosina[2], F. Gerenzani[2], N. Ludwig[3] and M. Gondola[3]
[1]ICVBC – CNR
[2]Dep. BEST Milan Polytechnic
[3]Dep. Of Physics – Milan State University

Abstract

The study presents two innovative application of Infrared Thermography (IRT) - “Spilling drop” and “Moisture ring”- aimed at detecting moisture diffusion in porous materials. IRT effectively contributed to evaluate both heat and vapour exchanges between stone surface and surrounding air, by localizing the diffusion of water through the porous system of the surface. Any change measured after the application of an hydrophobic product, should be related to the performances of the product itself. The methods were successfully used both in laboratory and on the field. Measures have been carried out before and after the application of well known water-repellent protective products (PMMA and PDMS) on Noto calcarenite, Dorata sandstone, Macedonia marble. Damp areas have been studied by IRT and by established methods; results have been used to evaluate the performances of water repellant treatments (capillary absorption, drying index, contact sponge, etc) allowing to compare the effectiveness of the innovative techniques with traditional ones.

Keywords: IRT, spilling drop, moisture ring, capillary absorption, evaporative flux, contact sponge

1 Introduction

As concerns performances of protective treatments, the most used instrumental techniques examine the porous building materials interaction with water [1, 2], colour evolution [3], product retained on the treated surface [4]. Recent works utilised Infrared Termography in evaluating thermo-igrometric exchanges in between the outer stone surface with its porous system and the environment [5, 6]. These exchanges are crucial in defining the risk condition for the conservation of an artwork surface and, when executed before and after a protective treatment, they help in understanding water transfer phenomena, close to the treated surface. The instrumental methods used so far, can easily be applied in laboratory on specimens purposely prepared; Karsten tube and contact sponge are two exceptions [7, 8] because the measurements could be carried out *in situ*, on areas having a diameter of only 6/8 cm, the tests have good accuracy if repeated because the replication of test gives a statistical base to the results. IRT could possibly overcome these limits and it could be set to study in the field and on a large surface the evolution of thermo-hygrometric exchanges, through two specific mechanisms: “Spilling Drop”, based in dropping a calibrated amount of water, avoiding any pressure, on an horizontal stone surface; “Moisture Ring”, based on the application of a soaked sponge, keeping it in contact with a constant pressure for two minutes [6]. In both these cases, IRT passive recapture allows to observe a water diffusion through outer surface and even in the underlying substrate of the stone. Laboratory tests have been carried out on three different stone (10 specimens for each stone); the results clarify the relationship among stone porosity, evaporation flux, water absorption by capillarity [10-11] and diffusion phenomena: the recaptures in the spectral band of Near Infrared (1-2.5 μm) allowed to distinguish liquid water distribution from the cooling effects due to its evaporation.

2 Materials

2.1 Stone materials

The experimental phase consisted in testing 30 stone specimens (5x5x2 cm) characterised by a different porosimetric features:

Noto calcarenite is mainly composed by micro-fossil shells with an irregular microstructure and with a spatic calcite cement in tiny crystals (97,5%); total open porosity is around 36% and it is characterised by macro-pores (around 70%) with 1-5 μm diamater. This stone shows an high water absorption by capillarity [10].

Macedonia marble is a dolomitic marble with saccaroid texture, mainly composed by dolomite (99%). Total open porosity is very low (0.5%) and macropores are the most present (70% of pores in the range 1-7.5 μm). Water absorption by capillarity is very low [10].

Dorata sandstone is a Miocene sandstone whith sparry calcitic cement and feldspar-quartz clasts; total open porosity is around 10% with meso and macropores, the pore diameter is in the range 0,001-7,5 µm. This stone is characterised by a mean water absorption by capillarity [10].

2.2 Treatments

Commercial treatments have been applied by capillarity (4h).

Paraloid B72: (Röhm & Haas), (EMA)/(MA), 5% in weight in ethyil acetate. Silirain 50: (Bluestar Silicones) (dimetyl-polisyloxane), 10% in weight in white spirit.

3 Characterisation of physical properties of outer layers of stone

3.1 Evaporative flux measures

Specimens were weighed during the evaporation after having saturated them with water, at equilibrium condition (RH 40%, T = 20°C). A desorption curve was obtained with an evidence of water exchange (liquid/vapour) between stone and air. Standard UNI-Normal 29/88 was modified as follows: every minute for 48h, the specimens were weighed in a climatic chamber, avoiding weight variations due to RH fluctuations. Evaporative flux curves have been obtained as a function of water content change; they are characteristic of a specific stone material and of its microstructure. After the comparison between the curves obtained before and after treatments, it is possible to evaluate the effects due to their application on the evaporation dynamic.

3.2 Spilling drop and moisture ring

Spilling drop test allows to measure absorption and diffusion of water (via IRT) at Air T= 23.5°±1° C, RH = 30±4 %. IRT shooting was carried out with a passive approach (frame rate 2 Hz; t=10 min): a calibrated drop (0,02 ml) was posed on the specimens surface using a micro-pipette. Moisture ring test is a combination of IRT and sponge contact test. The test provides a quantitative measurement of the absorbed water with the aid of a sponge (3 cm diameter) kept touching with stone surface under constant pressure; the sponge is soaked with 1.5 ml of water. the contact between stone and wet sponge has been 2 minutes long, while the surface has been kept horizontal [7, 8]. The researchers have been shooting a thermographic sequence after the application of the sponge/drop for 10 minutes, giving images of the evaporation/diffusion of the water poured out the sponge/drop to the surface. In both tests the water diffusion dynamic in the outer surface layers depends on the porosimetric features and on the hydrophobic performances of the treatment. Water evaporation caused a cooling in correspondence of damp areas; heat contrast between damp and dry areas is well established by IRT when evaporative flux is great enough to be measured.

4 Results and discussion

The adopted measures allowed to distinguish the different stone materials, their water exchange properties and the changes induced by treatments: porosity and the stone microstructure affect water absorption by capillarity, water diffusion and the subsequent evaporation mechanisms.

4.1 Contact sponge

The amount of water absorbed by Marble, Dorata Sandstone and Noto calcarenite by contact sponge methods stand in 1:5:80 ratio (Table 1). After the treatments, the researchers observed that:

- Marble: due to its extreme compactness no meaningful decrease in the amount of water absorbed was observed.
- Dorata sandstone: both the treatments caused a decrease in the amount of absorbed water about 80%.
- Noto Calcarenite: both the treatments caused a notable decrease in the amount of water absorbed (Silirain 50 = 97% and Paraloid B72 = 98%)

Table 1: Results of the water absorption test by contact sponge

Material	Total open porosity (%)	Water absorption Wa (g/cm^2 *min)		
		Untreated	Sil50	PB72
Marble	0,57	0,0005 ± 0.0001	0,0005 ± 0,0001	0,0003 ± 0.0001
Sandstone	10,70	0,0025 ± 0,0004	0,0005 ± 0.0001	0,0005 ± 0.0001
Calcarenite	36,00	0,0393 ± 0,0004	0,0008 ± 0,0001	0,0006 ± 0,0001

4.2 Measures of evaporative flux

Measures of evaporative flux on Noto Calcarenite provided higher values respect to the ones recorded on sandstone and marble; that value remained constant untill the water content was close to 7%. After the treatments, the amount of absorbed water firmly decreased; hence the evaporative flux was reduced to zero values. Both treatments negatively influenced the stone evaporating ability. The evaporative flux of Dorata sandstone was higher in the beginning, when most of the absorbed water evaporated; later the mechanism became similar to the marble one (quite null). Obtained measures after treatments allowed to distinguish perfomances of the two tested products as regards water absorption: application of Silirain 50 reduced the water content of 23% after imbibition, and the 76% of evaporative flux at saturation; a notable decrease was recorded at the beginning of desorption. The application of Paraloid B72 did not change the water amount after the imbibition, but the evaporative flux at saturation was reduced of 43% due to modified porosimetric features, induced by the product itself. The trend of the evaporation curves recorded before and after the treatment was quite similar, but it was reduced of about 50% with the ankle at about 2% of WC; hence it is argued that only little changes were produced both in the porosimetric structure and in the stone permeability (Fig. 1). During the first 24h the evaporation in marble specimens displayed the fastest kinetics due to the low amount of absorbed water and the characteristic porosity; in addition, sandstone showed a minor tendency in evaporation. Treatments application on sandstone and calcarenite lead to lower the natural evaporation features, with a worst performance as to Silirain respect to Paraloid (Table 2). The obtained data proved fruitful in characterising physical properties – before and after treatments - discriminating performances of the outer surface and bulk.

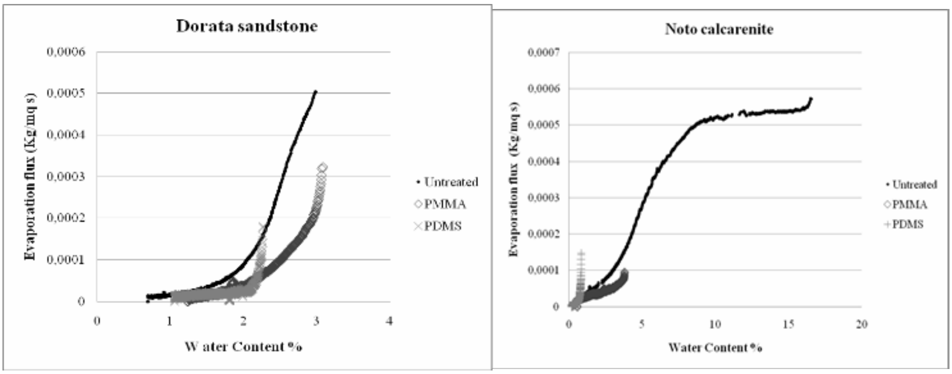

Figure 1: Evaporation flux of Dorata and Noto before and after treatment

4.3 Spilling Drop

Fig. 2 shows the differences in water diffusion on specimens surfaces before and after treatments. The geometry of the drop, immediately after deposition and at the maximum extension time, was characteristic of each stone. On marble surface the wet area was is the smallest among those tested; it showed regular shape and the halo, caused by the cooling effect, formed a tiny outline all around the drop itself. Hydrophobic treatments did not notably change the marble absorption abilities.

Table 2: Water content and evaporation flux values at saturation on different materials before and after treatment

Material		Saturation WC (%)	ΔW	Evaporation flux at saturation Φ_{ev} (Kg/m^{2}s x 10^{-4})	$\Delta\Phi_{ev}$
Marble	Untreated	**0,13** ± 0,06		**0,55** ± 0,48	
	Sil50	**0,13** ± 0,06	+0,00%	**0,17** ± 0,12	-69,09%
	PB72	**0,14** ± 0,08	+7,69%	**0,22** ± 0,19	-60,00%
Sandstone	Untreated	**2,81** ± 0,25		**4,38** ± 0,45	
	Sil50	**2,14** ± 0,20	-23,84%	**1,02** ± 0,52	-76,71%
	PB72	**2,84** ± 0,32	+1,06%	**2,48** ± 0,19	-43,37%
Calcarenite	Untreated	**15,38** ± 2,47		**5,36** ± 0,32	
	Sil50	**1,26** ± 0,24	-91,80%	**1,24** ± 0,23	-76,86%
	PB72	**2,86** ± 1,05	-81,40%	**0,87** ± 0,16	-83,76%

On sandstone the wet area was larger than the marble one, and it showed irregular outline and shape. After the treatments both shape and outline became regular. On Noto Calcarenite the wet area was the largest among those tested, with regular shape and outline. After the treatments the dimensions of the wet area notably decreased (61,5% as concerns Silirain 50 and 63,3% as to Paraloid B72). During the recapture time (10 min) no variations occurred in the wet area dimensions, giving the idea that both treatments mantain the protective effectiveness in short time (Table 3).

4.4 Moisture ring

After the application of contact sponge, the researchers recorded a sequence of thermal images at the frame rate of 1 Hz; the temporal evolution of surface temperature allowed to evaluate the water transport on the sample's surface because of the differences of the specific heat between water and stone materials. The morphology and the dimension of the wet area depended on the materials porosimetric characteristics and on water-repellency of the applied products (Table 4). The thermogram at maximum extension was utilised to characterize the materials, whilst the analysis of the entire thermograms sequence proved to be the best procedure in evaluating the effectiveness of protective treatments. On the marble surface the wet area corresponded to the sponge area; outlines were regular with a tiny ring due to stone cooling (Fig. 3a). Shape and dimensions of the moisture ring were due to the low porosity. Cooling effects on dorata sandstone showed the smaller moisture ring and the outlines of the wet area were totally irregular (Fig. 3b). On Noto calcarenite the wet area was the largest and the thermogram at maximum extension allowed to visualize the effects of a notable water absorption which caused great water spreading and consequently heat diffusion (due to the high evaporation rate) (Fig. 3c). After treatments, for all specimens of the test, the wet area was equal to the sponge one and no cooling allowed to discriminate the different superficial porosimetric features; actually sandstone displayed a greater variety in pores dimensions respect to Marble and calcarenite. The evaporation time was different due to the treatments proving useful to discriminate their performances; on the contrary the geometry of the wet area and its dimensions did not differ as to the applied products.

5 Conclusion

The procedures here discussed belong to three different analytical measurements, the coherence of obtained results allowed to appreciate the integrability of the used techniques. The measures of water diffusion by IRT were validated by the results of established gravimetric methods, that quantified .absorption and evaporation capabilities of stones before and after treatment. Moreover, coupling IRT and contact sponge method, allowed to pinpoint the factors that may be predominant for the identification of risk condition, for example the measure and distribution of pores in the superficial layer, where the cycles of water exchange are more active than underneath. The used methods permitted a qualitative, but pretty accurate, distinction of porosity in the superficial layer and allowed the evaluation of effectiveness of the treatments procedures. It is well known that decay processes usually begin in the surface layer, and the thermo-recordings of the contact sponge method interest exactly this layer. With a periodic application of this methods, and respecting a conservative protocol, the restorer/conservator acquires data useful to evaluate the effectiveness of the conservation operations and in preventing damages. Since the good results obtained in laboratory tests, the exportation of the technique in site is now at study. From the theorist point of view there are no contraindication but the firsts experiences showed that there are many limits and difficulties because the yard is a complex system where variables like climate, degradation and past restoration on the stone surface, play a fundamental role in the acquisition, elaboration and interpretation of dates.

Table 3: Average areas of the drops after their placing At1, at their maximum spreading At2 and percentage of area's increase ΔA

Materials		**At_1 mm²**	**At_2 mm²**	**ΔA %**
Marble	Untreated	15,2	19,5	27,0
	Sil50	16,1	17,5	9,10
	PB72	17,3	19,8	14,6
Sandstone	Untreated	16,9	35,3	109
	Sil50	15,1	15,3	1,51
	PB72	18,2	20,2	10,9
Calcarenite	Untreated	63,3	119,0	87,9
	Sil50	16,1	16,1	0,00
	PB72	15,4	15,9	2,98

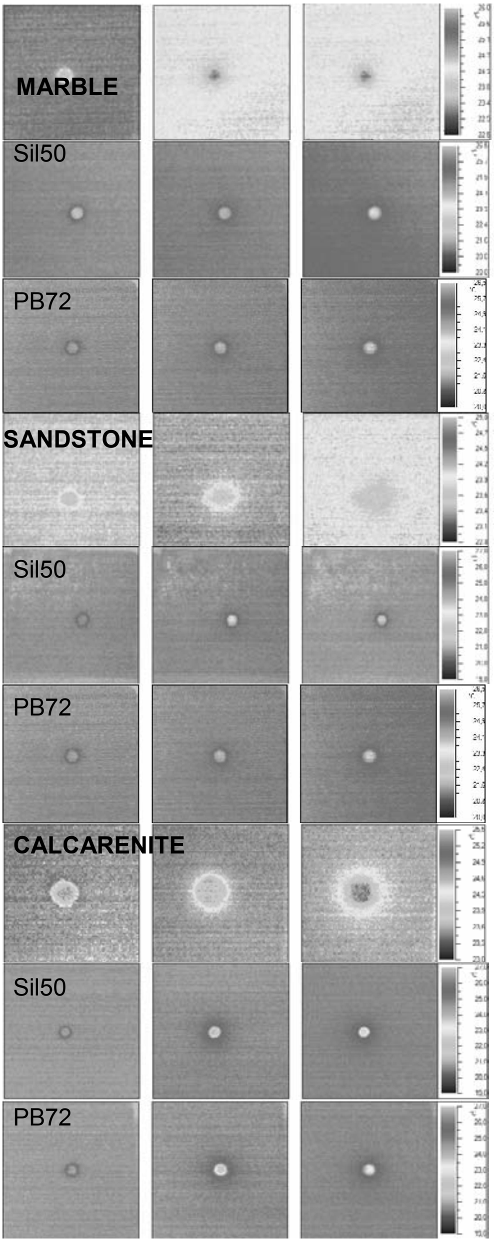

Figure 2: From left: initial, after 5 minutes and final thermograms after the dropping of the water drops on the surface. Ambient condition RH 30%, T 23,5°C, emissivity 0,89-0,95. Images have the same metric scale; the water content of the drops is the same (0,02 ml)

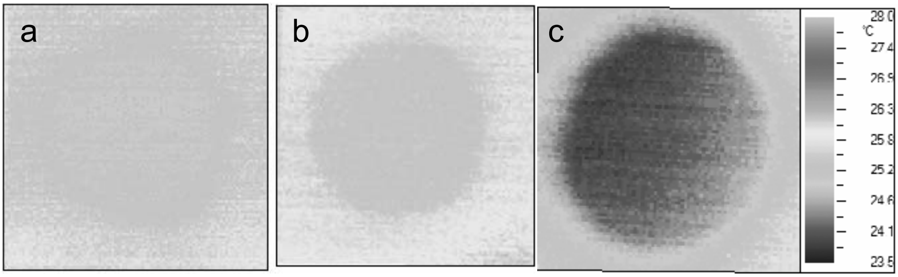

Figure 3: Moisture ring at maximum extension from left to right: marble (a), sandstone (b) and calcarenite (c) before the treatment. Ambient condition RH 30%, T 23,5 °C, emissivity 0,89-0,95. Images have the same metric scale

Table 4: Results of the Moisture Ring Test (A_1=starting area, A_2=maximum extension, MRA = moisture ring area, CSA = Contact sponge area, t_{ev}=evaporation time)

	Untreated	**Sil50**	**PB72**
Marble	A_1=879,3 mm^2 A_2=879,3 mm^2 ΔA=0% MRA ≈CSA regular geometry and shape Low absorption $t_{ev.}$=1:52 min	MRA ≈ CSA regular geometry and shape No absorption phenomena $t_{ev.}$=1:28 min	MRA ≈ CSA regular geometry and shape No absorption phenomena $t_{v.}$=2:06 min
Sandstone	A_1=851,8 mm^2 A_2=851,8 mm^2 ΔA=0% MRA <CSA irregular geometry and shape Low absorption $t_{ev.}$=6:50/>10 min	MRA ≈ CSA regular geometry and shape No absorption phenomena $t_{v.}$=2:02 min	MRA ≈ CSA regular geometry and shape No absorption phenomena $t_{ev.}$=2:01 min
Calcarenite	A_1=1263,2 mm^2 A_2=1534,6 mm^2 ΔA=+21% MRA >CSA regular geometry and shape High absorption $t_{ev.}$=>10 min	MRA ≈ CSA regular geometry and shape No absorption phenomena $t_{ev.}$=2:06 min	MRA ≈ CSA regular geometry and shape No absorption phenomena $t_{ev.}$=2:38 min

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