EFFECTS OF THERMAL CYCLES ON STONE DECAY

Massimo VALENTINI - Gianni SALA - Centro C.N.R. 'Gino BOZZA'

ABSTRACT

The paper reports some results of a series of enviromental measurements carried out on Palazzo Nicolaci placed in Noto (Siracusa) in the context of a research on the causes of decay of the stone employed in the town's ancient buildings. The measures show high and rapid variations of the surface temperature of the external walls exposed to sun radiation.

Such thermal variations were reproduced in laboratory on stone samples (taken from quarry) to assess their influence on stone decay. This paper shows the preliminary results of tests on two series of samples: one dry and one kept moist by imbibition. The authors measured some physical parameters (weight loss, porosimetric characteristics, surface imbibition capacity) and carried out some observations by scanning electron microscope.

1. INTRODUCTION

The town of Noto, located in the province of Siracusa, Sicily, Italy, was razed to the ground by an earthquake in 1693 and rebuilt, for the most part with local stone, on another site. Therefore, the results obtained in a study on the causes of the stone decay and restoration methods may be applied to almost all the town's buildings.

The C.N.R. Center " G. Bozza " approached this project from different points of view: the effects on the treatment of the material (Bocci *et al.* [1]), the water content in the wall buildings (Broglia *et al.* [2]), the material decay (Alessandrini *et al.* [3]) and the effectiveness of protective treatments (Alessandrini *et al.* [4]). This report deals with the influence of the thermal cycles induced by the effects of the daily insolation on the surface of the stone work.

2. CHARACTERISTICS OF NOTO STONE

The stone mostly used in the rebuilding of the town of Noto is a yellowish, porous, fossiliferous Miocenic calcarenite, locally called "pietra da intaglio". The stone shows clear elliptical, cilindric-shaped sedimentary structures (here called "tubuli") having the same petrographic, morphologic and physical characteristics as the stone itself.

The most evident and common form of decay of Noto stone is alveolization, which mostly occurs close to the area between the stone and "tubuli", as this zone is a preferential route for water evaporation, associated with a marked crystallization of salts. Crystallization causes the loss of cohesion in the microcrystalline matrix of the stone, which thus begins to pound round the "tubulo", to the point of the detachment of the material (Alessandrini *et al.* [3]).

3. RESULTS OF ENVIRONMENTAL MEASUREMENTS

The courtyard of Palazzo Nicolaci (size: 10 x 30 m) was chosen as the study site. The air temperature and relative humidity, together with the surface temperatures of the walls of the buildings surrounding the courtyard, were recorded for one year. The measurements of the surface temperatures were taken at two different heights from the ground (2 and 5 m) on different facing walls with sensors suitably shielded from insolation. The measurement probes used (copper-constantan thermocouples for the temperature and capacitive probes for relative humidity) were connected to a recorder which provided a graph showing the values over time and a printout of the corresponding numeric values every two hours.

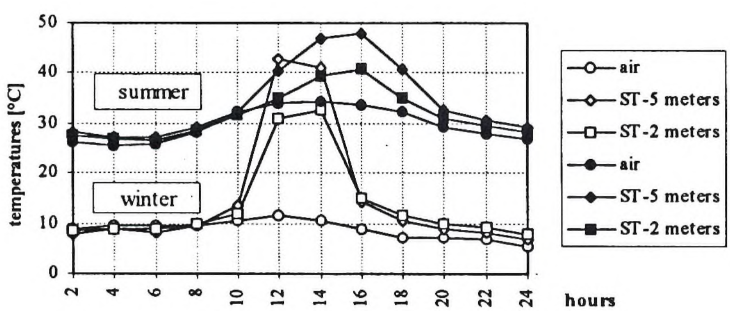


Figure 1. Air and surface (ST) temperatures

The measurements highlighted a typical phenomenon of all the buildings sited at latitudes in which insolation is high even in winter. This phenomenon, occurring only in the middle of the day, consists in a rapid vertical temperature gradient due to insolation, which particularly affects the surface layer of the walls. Marked changes in temperature of up to 30°C were recorded in the span of two hours, particularly on the walls facing south; the subsequent cooling was also very rapid. Figure 1 shows the air and wall temperatures taken at 2 and 5 meters from the ground, recorded in the months of January and July. High temperature gradients were recorded especially in the winter months because of the presence of two concomitant phenomena: the cooling of the wall at night and the perpendicularity of the sun rays against the walls.

The measurement of this type of phenomenon suggested the laboratory verification of the possible effects of these thermal cycles on stone decay.

4. LABORATORY EXPERIMENT

The experiment was conducted on 16 stone cubes (size 5x5x5 cm), taken from quarries near Noto.
The cubes were divided into two groups of eight samples each. The first group was subjected to thermal cycles as such (*dry series*), while the second was kept moist by imbibition (*moist series*) with the samples placed on a package of several sheets of filter paper laid on top of one another and immersed in deionized water. The water level was kept constant and never exceeded the upper edge of the paper package.
The decision to conduct thermal cycles on moist samples was prompted by the fact that the town buildings studied recorded a heterogeneous and high humidity content in their walls (the humidity values of Palazzo Nicolaci were between 4% and 20% by weight) (Broglia *et al.* [2]). This humidity is primarily attributed to capillary rising damp from the ground and, secondarily, to the formation of surface condensation (the measurements taken in the court of Palazzo Nicolaci during one year, recorded an amounting of condensation events to 2% of all the readings).

The thermal cycles were obtained by irradiating one of the sides of the cubes (in the case of the moist series the side opposed to that in contact with the water) by an infrared lamp (energy peak at 2.3 μm wavelength; maximum intensity 5 W/cm^2). The thermal cycle consisted in a heating phase of 30 minutes - during which the maximum temperature was reached on the surface of the samples - followed by a 90 minute cooling phase, at the end of which the samples were brought back to room temperature. The thermal cycles were repeated 1250 times.

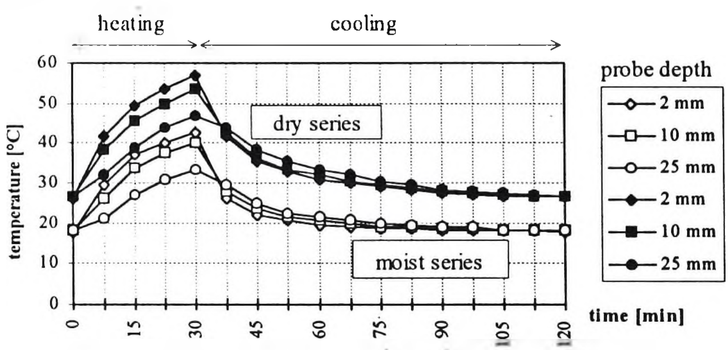


Fig. 2 Thermal cycle for dry and moist series and for different depth from irradiate surface

The temperatures reached in the samples during the thermal cycle were checked through a control cube in which thermocouples had been inserted at different depths from the irradiated surface (2 mm, 10 mm and 25 mm). The results of this verification are shown in Figure 2.
During the thermal cycles, the samples of the moist series, which are underwent continuous evaporation and subsequent imbibition, maintained a constant humidity content, equal to 20% by weight.

4.1 Verifications

The following control analyses and measurements were planned to verify the effects of the thermal cycles on the material:

- porosimetric analysis;
- weight loss;
- capillary water absorption;
- scanning electron microscope (SEM) observations.

4.1.1 Porosimetric analysis The porosimetric analysis (Normal [5]) was conducted on the same three samples of each series to guarantee homogeneous data in spite of the typical heterogeneity of the material. The measurements were taken at the beginning of the test, after 360 and 1250 thermal cycles. Each time, test specimens (1x1x1 cm in size) were taken along the plane perpendicular to the irradiated side of the cube at three different depths (1 cm, 3 cm and 5 cm). After the test specimens had been taken, the remaining portion of the same three samples continued to be subjected to thermal cycles.

4.1.2 Weight Loss At the beginning of the test, five samples from each group were weighed after being dried in an oven at 105°C, to evaluate the initial reference weight. The loss in weight was measured after 360, 612 and 1250 thermal cycles by weighing the samples (after drying) and comparing the values recorded with the initial reference weight.

4.1.3 Capillary Water Absorption The test of the capacity for water absorption by capillarity was conducted according to Normal Recommendation (Normal [6]), although the test time was limited to only five minutes. This duration was chosen to reduce the height of the water rising in the sample to better highlight the behaviour of the outermost layer in terms of imbibition. The measurement was also repeated on the side opposite to the irradiated face. The test was repeated after 360, 612 and 1250 thermal cycles using the same five samples subjected to the weight loss test.

4.1.4 Scanning Electron Microscope Observations The SEM observations were conducted at the end of the thermal cycles to verify any variation in the surface morphology of the samples. To this end, both the irradiated and opposite sides were observed.

5. Results and Discussion

5.1 Porosimetric Analysis

The results obtained on the samples prior to the thermal cycles confirmed the high heterogeneity of the total porosity values of Noto calcarenite (total porosity between 25% and 39%) already found in a previous study (Alessandrini *et al.* [3]).

The porosimetric distribution maintained a unimodal trend even after the thermal cycles with peaks in correspondence of the pores with diameters of 2 µm to 4 µm.

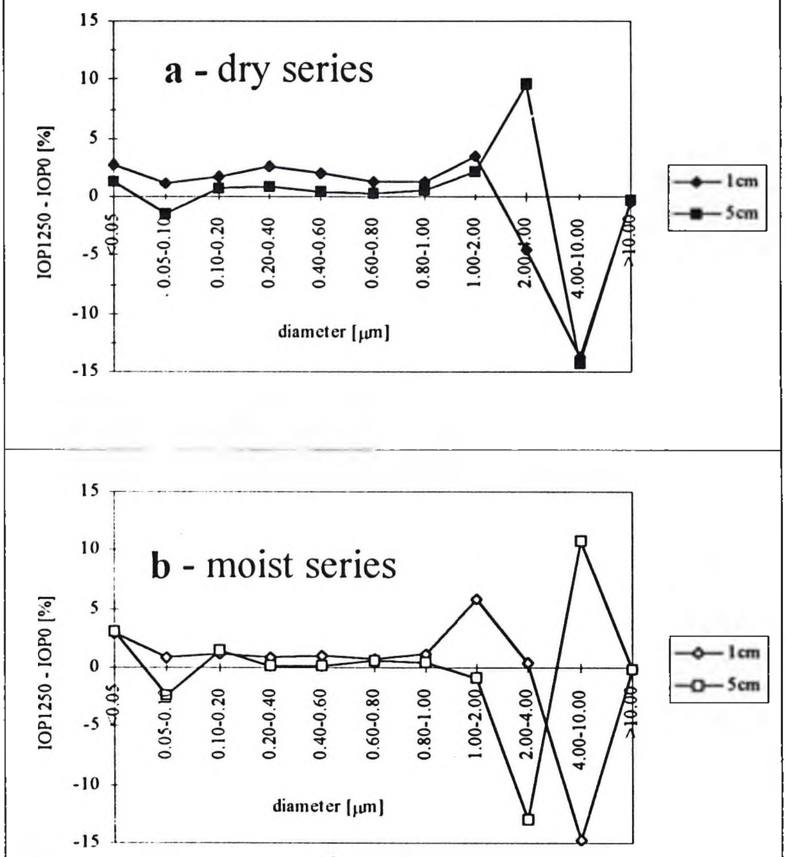


Figure 3 a-b Difference between integral open porosity at 1250 cycles (IOP1250) and before the test (IOP0) for different depthes.

After 1250 thermal cycles, the samples of the *dry series* showed a decrease in total porosity in the layer closer to the surface (-45%) and a slight increase in deeper layers (+15%). The outermost layer (1 cm) showed a slight increase in pores with diameters smaller than 2 µm and a marked decrease of the incidence of pores with diameters between 2 µm and 10 µm. Deeper layers (3 and 5 cm)

showed practically no variation in the porosimetric distribution for pores with diameter up to 2 µm, but an increase in the percentage of pores with diameters of 2 µm to 4 µm as a consequence of the reduction of pores with diameters of 4 µm to 10 µm (Fig. 3a).
At the end of the thermal cycles, the samples of the *moist series* showed an increase in total porosity in the layer at 1 cm (+13%) and a decrease in the deeper layer (-13%). The outermost layer showed a minimal variation of pores with diameters up to 1 µm, a percentage increase in pores with diameters between 1 µm and 2 µm and a marked reduction in pores with diameters between 2 µm and 10 µm. A decrease in pores with diameters between 2 µm and 4 µm was found in deeper layers as a consequence of the augmentation of pores with diameters of 4 µm to 10 µm (Fig. 3b).

The modifications induced by the thermal cycles cannot be interpreted on the basis of only the porosimetric characteristics, in part because these modifications may be confused with the material heterogeneity mentioned above.

5.2 Weight Loss

The loss in weight was negligible in the samples of the *dry series*, while it was more marked in those of the *moist series*. After 1250 thermal cycles, the percentage weight variation was found to be 0.03% in the dry series and 0.28% in the moist series. This suggests that the loss in weight was not due to the effects of the thermal cycles, but to the loss of material caused by the water dissolution of the carbonate component of the stone, a process favoured by the carbon dioxide present in the air.

5.3 Water Absorption by Capillarity

The values observed in the untreated material were comparable to those inferable by interpolation from the results presented in another work on the complete test of absorption by capillarity (Alessandrini *et al.* [3]).

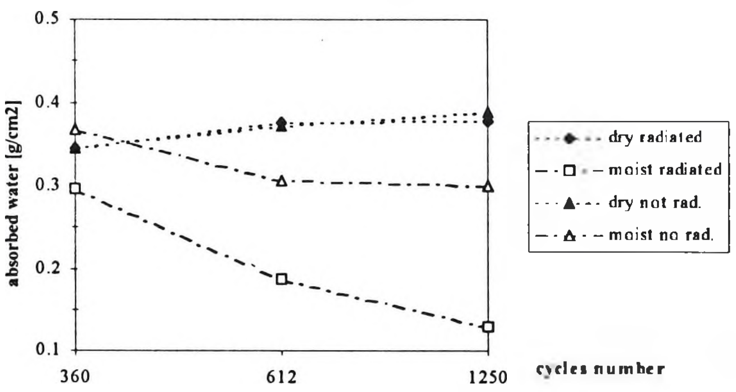


Fig. 4 Absorbed water

In the samples of the *dry series*, no differences were found between the values recorded on the irradiated surface and those recorded on the non-irradiated surface. On the contrary, in the samples of the *moist series* it was found that the irradiated surface absorbed less water than the non-irradiated surface and that the quantity of absorbed water tended to reduced in both the surfaces with the progress of the thermal cycles (Fig. 4).

5.4 Scanning Electron Microscope Observations

The surface morphology of the *dry series* did not show any modifications after the thermal cycles either for the irradiated surface (fig. 5a) or for the opposite (not irradiated) side (fig. 5b).

The morphology of the irradiated surface of the *moist series* appeared completely modified following the thermal cycles, i.e., much more compact (Fig. 5c) than the non-irradiated surface (Fig. 5d), and showed a clear network of microcracks.

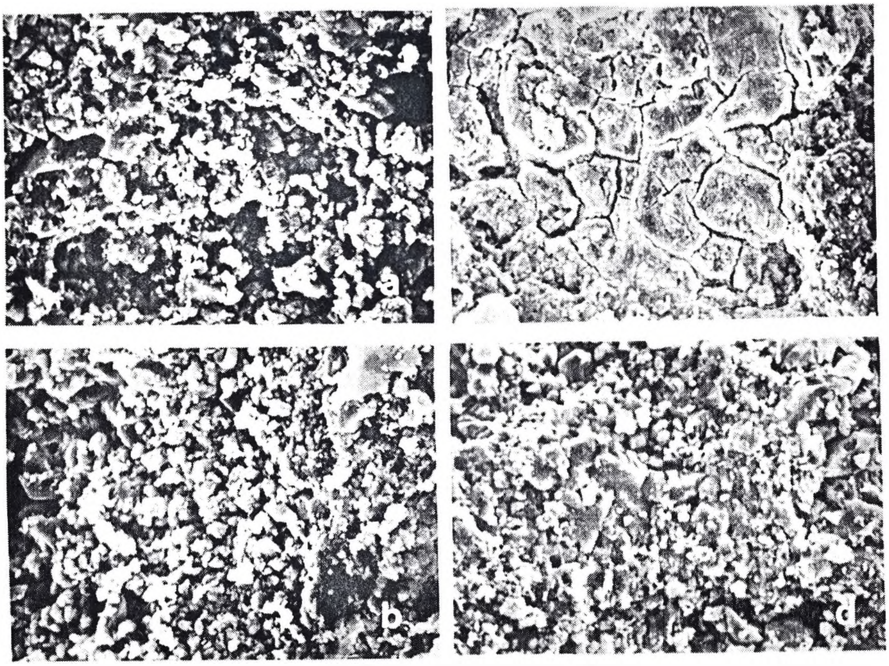
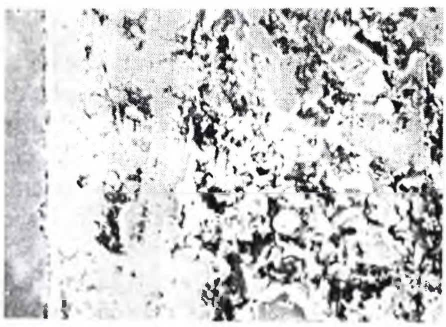


Figure 5 (500X) a) - b): dry series. c) - d): moist series.

Cross-section observations for the moist series samples, highlighted the presence of a compact layer about 20 µm in thickness (Fig. 6).

Figure 6. Cross-section of the moist series (150X)



5.5 Discussion

The greater compactness of the surface layer of the *moist series*, observed by the SEM, may be attributed to the following, consecutive, phenomena:
dissolution in water of the carbonate component;
migration of the solution towards the outer surface;
water evaporation accelerated by irradiation;
precipitation of calcium carbonate into the interstices.
The presence of a compact surface layer justifies the reduced water absorption by capillarity; this reduction would probably have been much higher in the absence of the microcracks observed on the surface.
The compact layer is too small to enable the determination of its influence on the porosimetric characteristics.

There is no compact surface layer in the *dry series* because of the absence of dissolution in water. The decrease in total porosity is probably due to the decay of crystalline framework caused by the temperature range which results in the occlusion of the pores of over 4 μm in diameter, but this, as shown by the measurements, does not modify the water absorption by capillarity.

6. Chromatic Alterations

Chromatic alterations, characterized by a rust-coloured tone, appeared on the irradiated surface of all the samples of the *moist series* from the first thermal cycles. As the thermal cycles increased, these alterations spread all over the sample surface (Fig. 7). A cross-section observation shows that chromatic alteration is only limited at the surface layer.

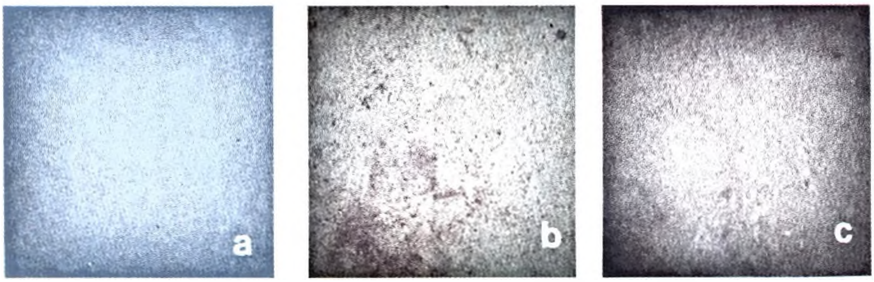


Figure 7. a) Surface at the begining of the test. b) After 360 thermal cycles c) After 1250 thermal cycles

Some analyses were conducted to identify the nature of these alterations. The XRD analysis showed traces of siderite (iron carbonate). The powder taken both from the areas with chromatic alterations and at a depth of 2 cm from the outer surface, where no chromatic alterations were observed, were subjected to atomic absorption spectrophotometry (AAS) following dissolution in HCl 1N. The results obtained showed that the iron concentration in the surface chromatic alterations was more than double that measured in depth (measured mean values: 0.256% Fe_2O_3 on the stains and 0.115% Fe_2O_3 in depth). These results may indicate the dissolution of iron carbonate, whose solubility in water is about five times higher than that of calcite, its subsequent migration to the outer surface, favoured by irradiation, and, therefore, the deposition of ferrous hydroxide (typically rusty in colour) by oxidation and hydrolysis.

7 Conclusions

The results of a first series of thermal cycles applied on Noto stone are presented. The analyses showed a modification of the physical and chemical characteristis of the samples of the moist series, in which the action of the thermal cycles was combined with the presence of water migrating through the sample. The number of thermal cycles was probably too low to cause marked modifications in the samples of the dry series.
This justifies the continuation of the test to analyze, also with other analytical tecniques more sophisticated than those here utilized, the way in which decay may progress.

It should be pointed out that the formation of an extremely thin, compact, rusty-coloured layer on the stone surface corresponds to the phenomenon occurring on the buildings of Noto more exposed to irradiation and which the local "masters" call *pietra allannata*, meaning a very thin but compact layer as that of a tin (called "lanna" in the local dialect). The local bricklayers assignes at this layer a capability of "protection" against the interaction enviromental parameters/stone.

Acknowledgements. The Authors wish to thank Chiara Colombo and Anna Maria Bocci for their collaboration in the measurements, as well as Rosario Papa from Noto for the supply of the material and the informations on local constructive technologies.

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