Construction and Building Materials 152 (2017) 907–922

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Damage monitoring on carbonate stones: Field exposure tests contributing to pollution impact evaluation in two Italian sites

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HIGHLIGHTS

- A field exposure test in two different urban environments is proposed.
- The effect of urban air pollution on three different stones was assessed.
- Physical features of stones affect the susceptibility to capture particulate.
- Trace element concentrations provide information about pollution sources.

ARTICLE INFO

Article history:
Received 23 January 2017
Received in revised form 16 June 2017
Accepted 4 July 2017

Keywords:
Air pollution
Building materials
Degradation
Particulate matter
Soluble fraction
Trace elements

ABSTRACT

During the last decades, many studies have been carried out on environmental monitoring in specific sites aiming at their protection and conservation; however, researches focused on the direct implications, in terms of quantitative evaluation of stone deterioration, of these monitoring actions are still scarce.

This experimental work aims at monitoring the degradation processes affecting historical buildings constituted by carbonate stones. Specifically, specimens of Carrara marble and two limestones largely used in the Sicilian Baroque architecture, namely Noto and Comiso stones, were exposed outdoor in two Italian sites (Catania and Palermo), which are characterized by different environmental conditions. The field exposure test lasted two years. Both the substrates and the deposited particulate collected at the end of the exposure underwent several analytical investigations including: i) optical microscopy, mercury intrusion porosimetry, colorimetric analysis and roughness analysis, for the characterization of stone substrates before exposure; ii) ion chromatography (IC), infrared spectroscopy analysis (FT-IR) and inductively coupled plasma mass spectrometry (ICP-MS), for the characterization of the particulate deposited on stone surfaces. The obtained results highlighted blackening and yellowing processes of the carbonate substrates, chiefly on those specimens exposed in Palermo where such processes were more noticeable. Furthermore, the high concentration of sulphates and heavy metals detected (mainly in Palermo site) pointed out that both cities are mainly interested by mobile emission sources such as vehicular traffic. Additionally, analyses demonstrated the key-role of intrinsic features of the lithotypes in the degradation processes. In this regard, the higher porosity and surface roughness of Noto stone explains the major deposition of particulate with respect to the other two examined carbonate rocks.

1. Introduction

Studies over the past few decades have explored the mechanisms that underlie damage of building materials exposed to outdoor polluted atmosphere [1,2]. These have typically been related to the dry and wet deposition of SO_2 and carbonaceous particles from polluted atmospheres and are known to lead to soiling and blackening of the stone surfaces implying also significant aesthetic undesirable changes.

It is well known that the reaction of SO_2 with the carbonate material leads to the formation of gypsum through the widely

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http://dx.doi.org/10.1016/j.conbuildmat.2017.07.048
0950-0618/

studied sulfation process, while elemental carbon (EC) in the aerosol is recognized as being responsible for soiling and blackening [3]. Afterwards it has been also highlighted that SO_2 has decreased from the mid-20th century until today and the decrease is expected to continue [4] arguing that the rate of decrease is foreseen to be more important in the east and south-east of Europe than in the west of Europe. Thus SO_2, while continuing to be an important damaging agent in the future, is expected to become relatively less significant [5]. Clear evidence has been given also that the contemporary atmosphere richer than in the past of NO_X and organic compounds deriving from vehicular traffic, is expected to imply a change in colour of the damage layers occurring on the built heritage with a shift from dark to greyish and brownish tones.

There is a wide international scientific literature on the diagnosis of the pollution impact on cultural heritage, where basically three main approaches have been followed:

- Comprehensive analysis of samples collected from monuments and historic buildings aiming at their characterization in terms of mineralogy, geochemistry, soluble and carbon fractions content [6–13].
- Test in simulation chamber with the aim of understanding the role of pollution and climate parameters (individually or in combination) in deterioration phenomena, and of evaluating the durability towards environmental impact of different building materials. The main limitation of this approach is the impossibility of reproducing real environmental conditions, as only extreme and unrealistic situations are created in order to reproduce damage in a relatively short time, considering very few variables that take part in the real scenario. However, it appears to work efficiently in giving outputs for describing in detail the chemical process at the basis of the effect of a specific parameter [14–16].
- Field exposure tests in order to have a more realistic picture of the ongoing deterioration phenomena on different building materials exposed to a specific environmental context or on the same material in diverse climate conditions [17–27]. Even though the first approach has been extensively used for the diagnosis of the state of conservation of a historic building or monument, field exposure tests have recently gained an increasing importance as a research methodology suitable for giving outputs with the final aim of proposing adequate solutions in cultural heritage conservation and maintenance. Concerning to that, in fact, there is the evidence that most of the work done through field tests, alongside simulations in climatic chamber, have contributed to develop damage and dose-response functions aiming at a quantitative evaluation of the effect of pollution and climate parameters on heritage materials, both organic and inorganic [4,28–30]. Additionally, it has been widely argued on the significance of deterioration modelling and its implication in formulating long-term strategies of heritage sites management.

During the last decades several papers have been also published reporting data on environmental monitoring in specific sites aiming at their protection and conservation; however, examples with an exhaustive discussion on the direct implications, in terms of quantitative evaluation of deterioration, of these monitoring actions are still scarce [31,32]. It is known that damage reflects the interaction over time between heritage materials and environment and that measurement of current atmospheric pollutants concentration cannot be enough for understanding what is going on the architectural surfaces.

The research work described here contributes to assess the effect of urban air pollution on three carbonate stones, i.e. Carrara marble and two limestones largely used in the Sicilian Baroque architecture, precisely Noto and Comiso stones, by performing field exposure tests. Additionally, the work aims at comparing in quantitative terms the entity of the deposition on the three examined stones and its progression over time in two different Italian sites located in Sicily, namely Catania and Palermo, which are characterized by diverse environmental conditions. The paper will discuss the quantification of soluble fractions (sulphates, nitrates and chlorides) and trace elements of the deposited particulate on the building materials under study and will examine the relation between the change of colour of the building materials and the environmental exposure.

2. Materials

144 specimens (48 for each lithotype) of Carrara marble (MC), Noto stone (NO) and Comiso stone (CO) of $5 \times 5 \times 2$ cm size were exposed at 24 m from the ground level in two Italian sites in Sicily, both located in areas strongly affected by pollution due to vehicular traffic: a) the ‘‘Dipartimento di Scienze Biologiche, Geologiche e Ambientali – Sezione di Scienze della Terra”, University of Catania; and b) the ‘‘Dipartimento di Giurisprudenza”, University of Palermo. The exposure height of specimens was chosen to avoid a direct contact with exhaust gases from vehicles and rather evaluate in both sites the contribution of different emission sources to the atmospheric pollution, i.e. mobile sources (e.g., cars, trucks, buses), stationary sources (e.g., factories, refineries, power plants) and natural sources (e.g. wind-blown dust, wildfires, volcanoes).

Suitable supports have been built to host samples with 2 different exposure conditions: sheltered and unsheltered from rain wash-out (Fig. 1). The exposure lasted 2 years from July 2011 to July 2013.

The stones have been selected mainly on the basis of their chemical composition, being carbonate stones highly vulnerable towards pollution impact, and because of their extensive use as heritage building materials. Specifically, Carrara marble is known to be one of the most valuable stones used in statuary and architecture in Europe [33–37], while Noto and Comiso stones are local lithotypes widely used in the eastern Sicilian Baroque architecture [38–42].

The main features of each lithotype at a macroscopic scale are the following:

1) *Carrara Marble:* Belonging to the Upper Triassic unit of the Apuan metamorphic sequence (Apuan Alps region, Northern Apennines, Italy), it is a medium-fine grained lithotype, with high compactness, white colour with greyish veins that are submillimetric in thickness and irregularly orientated.
2) *Noto stone:* Belonging to the Buscemi Member of the Palazzolo Formation in the Hyblean area, it is a calcarenite, yellowish-white to deep yellow at fresh cut erosion, with a medium-coarse arenitic size and tender texture. The structure is heterogeneous for the presence of cylindrical bioturbation (skolithos).
3) *Comiso stone:* Belonging to the Leonardo Member of the Ragusa Formation, in the Hyblean area, it is a well lithified, white-cream and fine-grained calcarenite, with tenacious consistency and homogeneous structure.

3. Methods

3.1. Characterization of stone substrates

Petrographic and physical characterization of stone samples before exposure was carried out by polarizing optical microscopy, mercury intrusion porosimetry, surface roughness and chromatic analysis. Both spectrophotometric and roughness analyses were implemented by using portable and non-destructive techniques (NDT).

- Petrographic analysis of stone samples was performed on thin polished sections through a Zeiss Axiolab microscope equipped with digital camera.
- Mercury intrusion porosimetry (MIP) analysis of substrates was carried out by means of an Auto Pore IV Micromeritics porosimeter, with maximum pressure of 400.000 kPa. Measurements were performed on three samples for each lithotype, all having the same weight (1.5 g) to standardize testing and minimize errors.