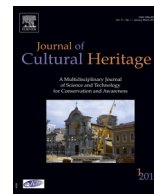




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Original article

Laboratory study of the sulfation of carbonate stones through SWIR hyperspectral investigation

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ABSTRACT

Stone-built Cultural Heritage is subjected to decay in urban environment over the centuries, due to surface interaction and reaction with natural atmospheric agents and, particularly in the last centuries, air pollutants. The Short wave Infrared (SWIR) characterisation of stone surface through portable instruments is attracting increasing interest in the field of Cultural Heritage. In this study, SWIR hyperspectral investigation of carbonate rocks, undergoing acid attack under laboratory conditions was performed with the aim of providing useful quantitative information on the degree of sulfation of the surfaces of carbonate stone. Six marble and six travertine specimens were attacked by aqueous solutions of H₂SO₄ at variable acid concentrations leading to the formation of gypsum. The reacted surfaces of stones were then investigated by a portable SWIR spectroradiometer. The resulting spectra were thus modelled through a full profile approach, in order to obtain a reliable and efficient fitting procedure. Thus, the SWIR characterisation of sulfated carbonate surfaces seems to be a promising, ready-to-use technique for monitoring the conservation state of carbonate stone monuments (e.g. facades, statues). This method could provide valuable support both for restoration practices and for continuous monitoring of stone alteration over time, when assessing the best strategy of intervention and conservation against sulfation processes of historical buildings.

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1. Research Aims

This work is focus on the capability of the hyperspectral technique to give information on the degree of sulfation of the surfaces of carbonate stone. This technique, recently introduced in the field of Cultural Heritage conservation, is completely non-invasive and allows to gain spectral information in both the visible (VIS) and near infrared (NIR) regions using a portable spectroradiometer (ASD Fieldspec[®] 3). The study is undertaken through the artificial alteration of carbonate stone specimen under laboratory conditions.

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2. Introduction

The impact of atmospheric agents and air pollution on Cultural Heritage stone-built materials is a serious concern, as it potentially threatens important parts of our history and culture. Atmospheric pollution, frost and salt weathering are traditionally considered the major causes of building stone decay [1]. Main damages include surface corrosion, soiling and bio-degradation, with consequent loss of details, blackening and formation of crusts on stone surfaces.

In recent years, major changes in both the sources and amounts of emissions of air pollution have deeply modified both the rate and the extent of damage of historical buildings. The proficiency of a combined study of meteorological parameters and air pollutant distribution to unravel the role played by climate changes in the weathering of stone buildings and monuments is attracting an increasing consensus among scientists [2,3]. Among the main components of air pollution, a reduction of the sulfur species (mainly SO₂) and, at the same time, an increasing role of nitrogen and

carbonaceous species (NO_x, nitrate, organic gases, elemental and organic particles) [4–7] have been recently observed.

In this study, we have examined one of the most diffused degradation processes affecting both natural and artificial carbonatic materials exposed to the urban atmosphere: the formation of sulfate-based deposits (i.e. “black crusts”) [8]. In particular, the volume increase due to the formation of gypsum from calcite [9] is the major cause of the development of cracks in the carbonate substratum of black crusts, often leading to ultimate degradation of stone materials.

The decreased content of acidic pollutants in urban atmosphere during the late 20th century is held responsible for the observed decreasing rate of formation of degradation crusts in the last years. According to Bonazza et al. [2], it can be envisaged that in the next future black crusts will be substituted by other forms of stone alteration driven by pollutants other than SO_x. In this scenario, black crusts themselves could paradoxically become part of our Cultural Heritage as witnesses of past atmospheric conditions of our cities, although presently sulfation is still among the most relevant alteration processes of carbonatic stone buildings in the urban environment [10]. Accordingly, the monitoring of stone alteration represents a key factor in the knowledge and prediction of the trend affecting the building stone in the XXI cent. urban framework [2,11]. The continuous monitoring of the conservation state of outdoor surfaces, including the qualitative and quantitative evaluation of the surface degradation, is then considered a good practice to understand stone damages and for planning and optimize conservative actions aimed to preserve historical buildings [12–14].

Continuous monitoring requires a non-destructive analytical approach and, possibly, a simple, low-cost and effective tool to study the decay processes affecting works of art.

Many non-destructive and non-invasive techniques like thermography [15], P-wave velocity measurements [16], Laser Imaging Detection and Ranging (LIDAR) [17] and Fiber Optic Reflectance Spectroscopy (FORS) [18] have been successfully applied in the last 20 years to monitor the degradation of works of art exposed outdoors. Traditional invasive or micro-invasive monitoring techniques like X-ray diffraction (XRD), Fourier-Transform Infrared spectroscopy (FTIR), Scanning Electron Microscopy (SEM) and ion chromatography still represent the most frequently used methods due to their accuracy, although the analyses are expensive and usually time-consuming. As a further drawback, an accurate and representative information about the general distribution of the degradation products and of the general conservation status of a work of art, through XRD, FTIR and SEM, implies a collection of a large number of samples in order to obtain a statistically representative physico-chemical characterization of the material substrate and an accurate monitoring of its conservation status.

Hyperspectral technique is an analytical method recently introduced in the field of Cultural Heritage conservation. Namely, hyperspectral analysis has been used to monitor the presence of both sulfates and oxalates on carbonatic stone materials of historical, artistic and architectural interest [19,20]. This technique allows a quick discrimination of different components (in rocks, soils, etc.) on the basis of their different spectroscopic signatures [21–23].

3. Experimental procedures

3.1. Materials and methods

Two different carbonate stones were used for this study: Carrara marble samples, from the Gioia quarry (Apuane Alps, northern Tuscany) and travertine from northern Latium. These two stones were chosen because they are among the most used for

Table 1
List of the investigated samples.

Rock type	Label	Sulfation procedure	SWIR	SEM-EDS	
Marble	M	No acid attack	X		
	M01	1 h in H ₂ SO ₄ 0.1 M	X		
	M03	1 h in H ₂ SO ₄ 0.3 M	X		
	M1	1 h in H ₂ SO ₄ 1 M	X		
	M2	1 h in H ₂ SO ₄ 2 M	X		
	M4	1 h in H ₂ SO ₄ 4 M	X		
	M5	1 h in H ₂ SO ₄ 5 M	X		
	M1SC	1 h in H ₂ SO ₄ 1 M		X	
	M2SC	1 h in H ₂ SO ₄ 2 M		X	
	M5SC	1 h in H ₂ SO ₄ 5 M		X	
	Travertine	T01	1 h in H ₂ SO ₄ 0.1 M	X	
		T03	1 h in H ₂ SO ₄ 0.3 M	X	
		T1	1 h in H ₂ SO ₄ 1 M	X	
T2		1 h in H ₂ SO ₄ 2 M	X		
T4		1 h in H ₂ SO ₄ 4 M	X		
T5		1 h in H ₂ SO ₄ 5 M	X		
T1SC		1 h in H ₂ SO ₄ 1 M		X	
T2SC		1 h in H ₂ SO ₄ 2 M		X	
T5SC		1 h in H ₂ SO ₄ 5 M		X	
Gypsum		gy1	No acid attack	X	

ornamental purposes in the architecture of central Italy, since the Roman age.

Six specimens of each lithotype (M01, M03, M1, M2, M4, M5 and T01, T03, T1, T2, T4, T5), obtained after cutting small parallelepipeds (about 5 × 5 × 1.5 cm in size) from a large stone sample, were used for the acid attack (at different acid concentrations: see below) and subsequent SWIR investigations (Table 1). In addition, three specimens of marble (labelled as M1SC, M2SC, M5SC) and three of travertine (labelled as T1SC, T2SC, T5SC) (Table 1), smaller in size (cubes of side 2.5 cm) were investigated by SEM-EDS after acid attack carried out with aqueous solutions of H₂SO₄ at different concentrations.

The calibration of the SWIR spectroradiometer for this study requires the use of suitable materials as reference standards for the polycrystalline calcite and gypsum phases. A sample of gypsum (gy1), obtained by grinding and sieving to a particle size < 15 μm a single crystal of gypsum, and of a calcitic marble specimen (M, from the Gioia quarry, Apuane Alps, Italy) were thus selected as internal standards for gypsum and calcite, respectively.

The sulfation of the specimens was carried out through acid attack under ambient conditions (T = 20°C). Aqueous solutions of H₂SO₄ were prepared at different molar concentrations (from 0.1 to 5 M, Tab. 1) and each sample was submerged half-height in one of these solutions for one hour (Fig. S2). The specimen was then dried for 3 days at room temperature (around 20°C); then, it was maintained under vacuum at 60°C for 3 days and put in a dry box containing anhydrous calcium chloride until a constant weight was reached. Then the total amount of gypsum formed on each sample was calculated as follows:

$$n = \frac{\Delta W}{MW_{gy} - MW_{cc}}$$

Where:

n (in mol) is the total amount of gypsum formed on the surface of each sample, ΔW is the difference of sample weight before and after the H₂SO₄ attack; MW_{gy} and MW_{cc} are the molecular weights of gypsum and calcite, respectively.

The SEM-EDS analysis was carried out on carbon-coated samples in order to verify the presence of gypsum, to measure the thickness of the sulfated layer, and to evaluate the change in morphology, grain size and distribution of the gypsum crystals as a function of H₂SO₄ concentration. Besides conventional samples, exhibiting the sulfated surface, cross-sections were also realised. A Scanning Electron Microscope ZEISS EVO MA 15, operating at 20 kV

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