

Study of the catalytic action of heavy metals to understand the phenomenon of sulphation and the formation of black crusts

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Abstract – The degradation of cultural assets exposed in out-of-door environments is a continuous and irreversible phenomenon that is largely accelerated by anthropogenic pollution. Various phenomena of degradation can develop on stone surfaces among which one of the most important is the formation of black crusts that are created in areas protected from runoff. The development of these degradation patinas is very complex and understanding their genesis could be fundamental in preventing the decay of monuments. This research shows the results of a second exposure campaign in accelerated ageing chambers in order to understand the role of catalysts that trigger the sulphation process and the formation of black crusts. This study was developed by analyzing samples of Carrara marble treated with metal cation solutions and PM 2.5 that were exposed for three weeks in corrosion and irradiation chambers.

I. INTRODUCTION

This research focused on the process of black crusts formation, an important degradation phenomenon that affects much of the artistic heritage exposed outdoors. On this regard, heavy metals and carbon particles present in polluted environment seem to be involved as catalysts in the sulphation process. This consists in the formation of sulphuric acid (H_2SO_4) from wet atmospheric sulphur dioxide (SO_2) leading to calcium sulphate dihydrate (gypsum, $CaSO_4 \cdot 2H_2O$) after interaction with calcium carbonate ($CaCO_3$, the stone substrate which the monuments are made of). Hence, the sulphation process can be favoured by some factors acting as catalysts both for the reaction itself (H_2SO_4 and $CaCO_3$ interaction) and especially for the preceding step related to the formation

of sulphuric acid by atmospheric sulphur dioxide oxidation. As aforementioned, these catalysing factors include the presence of various heavy metals adsorbed on carbonaceous particles, the role of which is still unclear.

The study of the effect of various pollutants, including metal cations, on the artistic and cultural heritage is of great global interest. In this context, two main investigative approaches have been adopted as reported in the literature: the first one consisted in chemical analyses of the actual black crusts formed on monuments, sculptures and historical buildings [1-14]; in the second approach, an experimental simulation of black crusts formation was carried out. In detail, regarding this second strategy, two different ways could be followed. As to the first route, samples were exposed outdoors in strategic/precise areas promoting black crusts [14-18], while the second way employed climate simulation chambers, also known as accelerated weathering chambers, where the samples underwent accelerated aging to reproduce the real damage in a short time [19-20].

In the present study, the second experimental approach was chosen employing two climate simulation chambers. In the “corrosion chamber” proper amounts of sulphur dioxide and humidity were set up; in the second chamber, xenon arc-UV radiation was supplied in order to simulate the sunlight irradiation naturally falling on monumental stone during the day. Properly treated marble samples were settled inside the chambers for assessing the catalytic action of metal cations commonly present in atmospheric particulate matter (PM 2.5).

The first experimentation campaign involved a single exposure in accelerated aging chambers (4 weeks with high concentration of SO_2) which highlighted the complexity of sulphation process [20]. Although some

conclusive considerations could be drawn, no univocal evidence on the role of the catalysts came out from this initial study.

Therefore, we decided to carry out a second experimentation campaign (3 weeks, with a SO₂ concentration twenty-fold lower than the first one). The aim was to better discriminate the catalytic role of individual metals thus confirming certain hypotheses from the first monitoring campaign, such as:

- some metal cations (Pb²⁺, Cu²⁺, Cr³⁺) showed greater catalytic activity than the others;
- different combinations of metal mixtures displayed greater synergistic effect in terms of gypsum formation;
- the samples treated with PM 2.5 led to chalk concretions reminiscent of real crusts at the end of the experiment.

Herein we report the novel results from the second exposure campaign. The chemical-physical characterization of the various samples was performed in both the pre-exposure and post-exposure steps using various analytical methods such as: observation with a stereomicroscope, SEM-EDX (scanning optical microscopy with energy dispersive spectroscopy) analysis, colorimetric analysis, IC (ion chromatography) analysis and analysis using XRPD (X-ray powder diffraction).

This research work is part of a broader interdepartmental project of the University of Milan, entitled SciCult, (Call SEED 2019 - "Mathematical modelling and scientific analysis for the CULTURAL HERITAGE: prediction and prevention of chemical and mechanical degradation of monumental stones in outdoor environments"), where the final objective will be to create a mathematical model for the prediction of the formation and development of black crusts in relation to a given environmental context.

II. MATERIALS AND METHODS

As previously done for the first exposure campaign [20], samples of white Carrara marble (3x3 x1cm, a total of 88) covered with graphitic carbon, to simulate the elemental carbon present in atmospheric pollution, were treated with aqueous solutions at appropriate concentrations containing the metal cations such as: Fe³⁺, Cu²⁺, Mn²⁺, Pb²⁺, Cr³⁺, V⁵⁺. Table 1 shows the concentrations of metal salts and oxides deposited on the specimen surfaces. The concentrations were identified by analysing particulate matter (PM2.5) collected on quartz filters in the city of Milan [21-22].

Table 1 Concentrations of metal salts and oxides deposited on the specimen surfaces.

Metallic cations	Concentration / ppm	Calts and oxides used
Iron III	2000	Fe ₂ O ₃
		Fe(NO ₃) ₃ ·9H ₂ O
Copper II	100	CuCl ₂ ·2H ₂ O
Manganese II	200	MnCl ₂ ·4H ₂ O
Lead II	70	PbCl ₂
Chrome III	40	Cr ₂ O ₃
Vanadium V	30	V ₂ O ₅

The solutions contained either mixtures of three or all the metals (M1= Fe³⁺, Cu²⁺, V⁵⁺; M2= Fe³⁺, Mn²⁺, Pb²⁺, Cr³⁺; M3= Fe³⁺, Cu²⁺, Mn²⁺, Pb²⁺, Cr³⁺, V⁵⁺).

Together with these samples, other samples were prepared in which atmospheric particulate matter (PM2.5) extracted from quartz filters sampled in the city of Milan was deposited. The extraction procedure from the filters was performed as reported in the literature [21-22].

In particular, in order to better simulate the real ageing process but in a relatively short time, the use of a corrosion test chamber in humid atmosphere was planned (introduction of SO₂), in line with what has been studied in the literature [23-29]. Furthermore, the simulation of solar radiation conducted in a special chamber (equipped with three xenon lamps) is of particular importance in the exposure cycle.

Indeed, the increase in material temperature, which normally occurs in real situations due to exposure to sunlight, could influence the catalytic mechanism of certain metal cations according to the well-known Arrhenius equation [30].

The exposure cycle involved:

- 48 hours (2 days - 4 cycles) of corrosion in a humid atmosphere (80±10%) with sulphur dioxide;
- 24 hours (1 day) of exposure to xenon arc UV light;
- 72 hours (3 days - 6 cycles) of wet atmosphere corrosion with sulphur dioxide;
- 24 hours (1 day) exposure to xenon arc UV light.

The exposure cycle was applied for a total of three times, i.e. three weeks, at the end of which sampling was performed.

The accelerated aging chambers used were available at Innovhub Stazioni Sperimentali per l'Industria S.r.l. (Milan, Italy).

Figure 1 shows some samples taken from the chambers after 3 weeks of exposure.

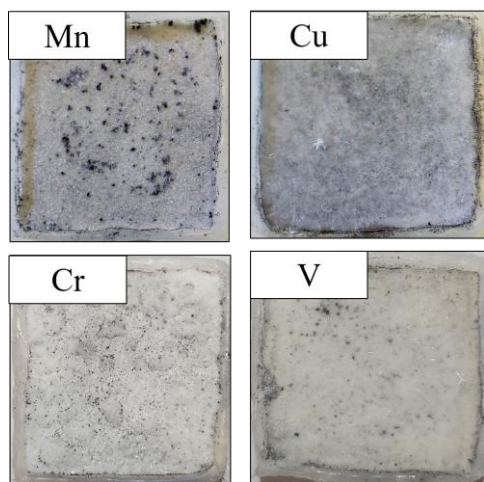


Fig. 1. Samples treated with Mn, Cu; Cr, and V solutions taken from the accelerated ageing chambers after three weeks of exposure.

The samples were characterized in both the pre-exposure and post-exposure phases through a multi-analytical approach in order to assess in detail the degradation process induced by sulphation on the surface. The methods used are:

- Stereomicroscope Sicher Milano with fixed binocular head inclined at 45 °, WF 10x eyepieces, 1W LED incident and transmitted illumination and 1x magnification.

- Colorimetric analyses were carried out by means of a Konica Minolta CM 2600d portable spectrophotometer, referring to the CIE L* a* b* chromaticity diagram and the NorMal 43/93. L* is luminosity or lightness, which varies from black (value = 0) to white (value = 100); a* ranges from +a*(red) to -a*(green) and b* varies from +b* (yellow) to -b* (blue).

- SEM-EDX was performed with a Hitachi TM1000 equipped with an energy dispersive X-ray spectrometer (Oxford Instruments SwiftED). The spectra were directly acquired on the surface since no metal coating was required in this case to analyse non-conductive samples.

- Ion chromatography (IC) was employed for the quantification of the main inorganic constituents of the deposits. About 2 mg of powder, collected in accordance with our previous work [35], was placed in a test tube and treated with 10 mL of Milli-Q water. The solutions were put in an ultrasonic bath for 1 h, then centrifuged for 30 min and injected for IC analyses. Measurements were carried out by using an ICS-1000 HPLC system equipped with a conductivity detector.

- The crystalline phase composition of the powders was determined by X-ray diffraction (XRD) by means of a Rigaku Miniflex 600 diffractometer

performing a continuous scanning using a randomly oriented powder mount.

III. RESULTS AND DISCUSSIONS

In both the first and second exposure campaigns, the complexity of the sulphation process and the formation of black crusts was highlighted. It was observed that some metal cations activate the catalytic process faster than others. The different combinations of metal mixtures, with which some specimens were treated, show a high synergistic effect in terms of gypsum formation (mainly in the last weeks). The formation of gypsum over time affects the degradation of the stone substrate and this is higher for some specimens. Due to SO₂ concentration decrease, the sulphation process could be actually slow down and this allowed to distinguish the catalytic action of the individual selected metals better than during the first campaign.

The results obtained using a stereomicroscope (Fig. 2) show that almost all of the samples displayed the formation of gypsum crystals on the surface from the first and the second week. In the third week, the samples developed small variations in the formation of gypsum compared to the other weeks; in fact, compacted acicular crystals were observed that originated concretions scattered heterogeneously on the analyzed surface.

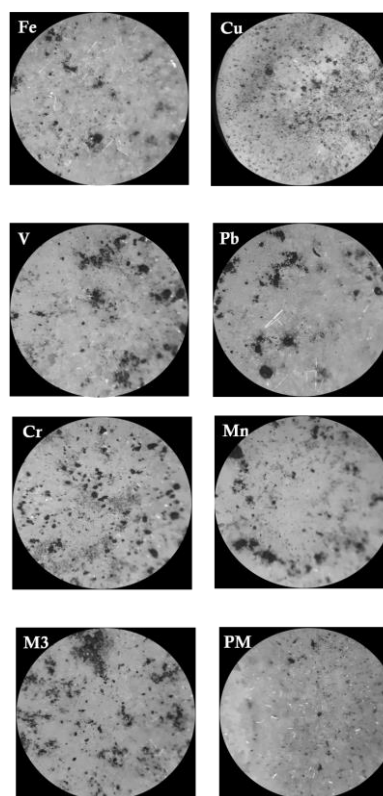


Fig. 2 Stereomicroscopic observations of samples taken during 3 weeks of exposure.

In particular, the most evident results were obtained from the observations of the surface crystals performed by SEM-EDX. The analysis led to characterize the crystalline dress of the gypsum; in fact, the following crystalline dresses could be recognized: acicular, lamellar, swallowtail and rosette concretions. Specifically, the observations revealed a similarity between some metals, in particular the specimens with manganese and copper are characterized by the presence of rosette concretions and lamellar habit, the specimens with iron and lead by very long and thin needle-like crystals and, finally, the specimens treated with chromium and vanadium display extended dovetail crystals that are organized in a rosette form (Fig.3).

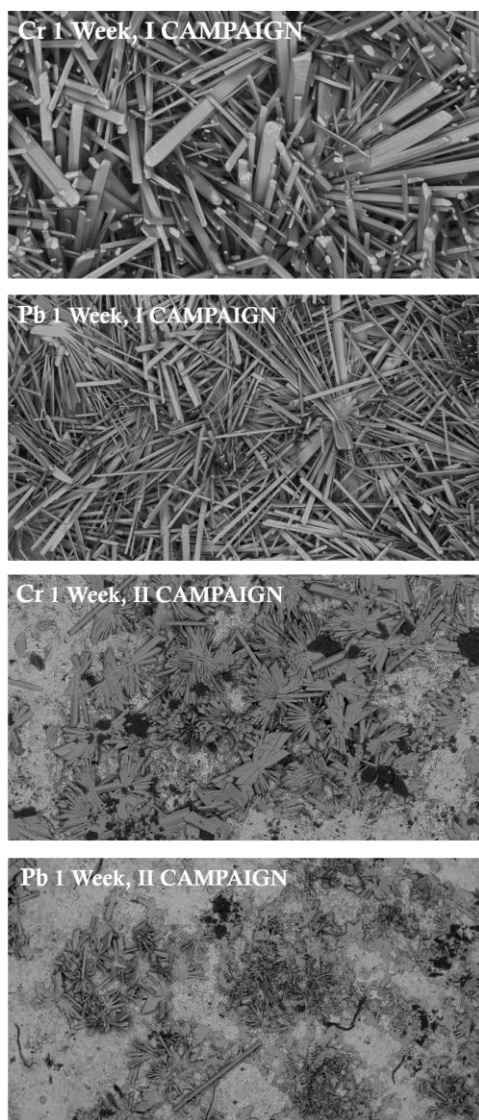


Fig. 3 Crystal images observed by SEM-EDX of some samples.

These differences might be related to the sulphation process. Accordingly, metals producing needle-like

crystalline garments might tend to sulphate faster than samples in which the formation of lamellar or swallowtail crystals is observed, whose crystals seem to organize themselves better on the surface forming small rosettes. Furthermore, over the three different weeks of exposure, the sulphation was more concerned with the thickening of crystals formed in the previous weeks and less with the nucleation of new crystals. The mixtures (in which some metals or all those selected are present together) show the different crystalline dresses that were observed for the specimens treated with the individual metals, while the samples treated with PM 2.5 displayed both a higher number of crystals and the presence of all the crystalline dresses observed for the samples treated with the individual metals. Moreover, at the end of the third week, the surfaces of the samples treated with the M3 mixture (all metals included) were similar to the samples treated with PM 2.5. The analyses conducted on the "blank" specimens show the development of much slower and less sulphation than the treated samples.

Colorimetric analysis, in terms of the change in ΔL^* (increase in brightness), displayed an increase in this coordinate, probably attributable to the formation of gypsum. An increase in the ΔL^* parameter was observed in all samples during the third week, ascribed to an increase in white gypsum crystals on the surface (as observed by stereomicroscope investigations) (Fig. 2).

From ionic analysis is evident that all samples display high sulphate values as early as the first week. This seems to suggest that the various metals used, individually or in a mixture, activate the formation of gypsum on the surface early on. An increase in the concentrations of sulphate ions was observed in the last week of testing for some samples (Cu^{2+} and Cr^{3+}), suggesting that the catalytic effect of these metal cations may be long-lasting. A higher concentration of sulphate ions was registered for samples treated with the M1 mixture and lower for M3 differently from the first exposure campaign [20].

Under these new experimental conditions, the Fe^{3+} -treated samples seem to be the most catalytically active, compared to the first monitoring campaign.

Also, for this second exposure campaign, the samples treated with PM 2.5 show more sulphation than all the other samples.

Finally, the XRPD analysis was performed to identify the crystalline phases present in the different samples. The results displayed that the powders have the mineralogical characteristics of calcium sulphate dihydrate with the relative characteristic peaks and calcium carbonate with less intense peaks.

IV. CONCLUSION

This study focuses on the sulphation process evaluation

by heavy metal catalysts triggering the formation of black crusts on marble samples inside climatic chambers. The ultimate aim of this research, in fact, is enabling the prediction of outdoor damage on artistic heritage by mathematical modeling presently underway.

The results so far achieved led to some important information on the sulphation process by metal catalysts such as:

- some metal cations activate the sulphation late but their action is constant over time (metal cations Cu^{2+} , Cr^{3+});

- a different catalytic action of the mixtures was observed (M1 more active, M3 less active);

- Fe^{3+} appears to be the most catalytically active, compared to a previous monitoring campaign [20]. This could be attributed to the different experimental conditions, which were less harsh and more real;

- the most advanced sulphation process was observed for the samples treated with PM 2.5.

Further mathematical and statistical studies on both the first and second exposure campaigns are currently underway and will be used to create a mathematical model to predict the formation and development of black crusts for a given site in relation to its air pollution.

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