2022 IMEKO TC-4 International Conference on
Metrology for Archaeology and Cultural Heritage
University of Calabria, Italy, October 19-21, 2022

Climatic chamber tests to evaluate the catalytic action of heavy metals in the sulphation process

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***Abstract* – Research conducted on the degradation of cultural and architectural heritage caused by the deposition of air pollutants indicates that both sulphur dioxide and particulate matter produced by the combustion of fossil fuels are the main agents responsible for the deterioration of carbonate materials. The main chemical degradation process is the sulphation of the substrate which consists in the initial conversion of sulphur dioxide (SO_2) into sulphuric acid (H_2SO_4) and the subsequent reaction of sulphuric acid with calcium carbonate. This leads to the formation of black crusts, which are composed of gypsum inside which particulate matter is embedded. Heavy metals adsorbed on the carbonaceous particles enable the sulphation of the substrate by acting as catalysts in both stages of the process. This research aims to evaluate which heavy metals activate the sulphation process by carrying out targeted exposure tests in climatic chambers.**

I. INTRODUCTION

In recent decades there has been a rapid deterioration of the artistic, cultural and environmental heritage. The deterioration of the materials is a complex phenomenon attributable to various factors, both natural and anthropogenic. Usually it occurs gradually, but irreversibly, and begins at the very moment in which the work of art is created.

The synergistic action of the various factors often involves both aesthetic and structural damage to the original material, which can compromise the perception of the work of art itself and cause its decay.

The process of degradation and alteration is mainly activated by exogenous agents, of physical, chemical and/or biological nature that act in a correlated way; instead, the response of the material to the attack of these agents depends on endogenous factors, such as the type of rock, its origins, its composition, its structure. Furthermore, the presence or action of physical agents also favours chemical degradation, which induces deep changes to the original material, leading to the total decay of the work in the most serious cases.

Atmospheric chemical agents are of both natural (for example the products of chlorophyll photosynthesis, volcanic eruptions, and sea salt), and anthropogenic (such as the products of industrial processes, vehicular traffic, domestic heating) origin. Among the various materials for artistic and architectural use, stones of carbonate nature (such as marble, limestone, dolomite) gain a good relevance, especially in the European area.

Therefore, knowledge of how atmospheric pollutants that affect the processes of deterioration and alteration of works of art is particularly important for their protection and for the choice of appropriate materials to be used for the construction of new structures.

In particular, the researches carried out on the degradation of carbonate materials show that they are particularly susceptible to the presence of water and to the deposition of sulphur dioxide (SO_2) and particulate matter (PM) produced by the combustion of fossil fuels (present in high concentrations especially in urban environments).

The main sources of atmospheric sulphur produced by anthropic activities are, in addition to the already mentioned fossil fuels such as coal and oil, the smelting processes of non-ferrous minerals. During these activities, the sulphur present as an impurity is oxidized to sulphur dioxide (SO_2).

From the point of view of the degradation suffered by carbonate materials, limestone stones are subject to the attack of water and sulphur dioxide which, through the sulphation reaction, transform calcium carbonate into gypsum (calcium sulphate dihydrate). This phenomenon under certain conditions (such as for example the protection of the surface of interest from strong washout and the presence of atmospheric pollutants which give it its characteristic colour) is at the basis of the formation of black crusts [1-4].

Furthermore, given the good solubility of gypsum, if the material is very porous, the attack can occur in depth causing, in a short time, its disintegration; if, on the other hand, the material is compact (such as marble), the deterioration mainly affects the surface, making it subject to dissolution by washing away or to the formation of encrustations (black crusts) in areas protected from washout.

During the sulphation process other atmospheric components are also involved and play an active role in the catalysis of this reaction. Among these, the suspended solid particulate composed of metals and metal oxides, silica and silicates, saline compounds such as sulphates, chlorides and nitrates and heavy hydrocarbons, is of particular importance [5-9].

This type of deterioration has always been the object of various studies [10, 11], being one of the most widely present and inevitable degradation phenomena concerning the world's artistic and cultural heritage. In order to better preserve the exposed surfaces over time, a continuous study is fundamental aimed at unveiling the mechanism of black crusts formation and the role of the various protagonists that are part of this process.

In this context, our work has focused finding the possible catalytic action carried out by some metal cations, such as Fe^{3+}, Cu^{2+}, Mn^{2+}, Pb^{2+}, Cr^{3+}, V^{5+}, present in the atmospheric particulate matter, through the exposure of marble specimens in climatic chambers for artificial aging. This work is part of the broader interdepartmental project of Milan University (Università degli Studi di Milano), called SciCult, SEED 2019 Call for the "Mathematical modeling and SCIentification analysis for CULTURAL heritage: prediction and prevention of the chemical and mechanical degradation of monumental stones in outdoor environments" conducted through a network among the Departments of Mathematics, Chemistry and Computer Science.

II. MATERIALS AND METHODS

The choice of the metals was performed on the basis of previous literature studies [12-16]. The chosen ions are the ones known to facilitate the oxidation of S(IV) oxide. In addition, stock solutions composed of mixtures containing some ions or all of them together were also prepared. The selected cations were: Fe^{3+}, Cu^{2+}, Mn^{2+}, Pb^{2+}, Cr^{3+}, V^{5+}. The concentrations to be deposited on the surfaces of samples were calculated based on the data from urban particulate matter (PM 2.5 sampled on filters in the city of Milan). Specifically, three mixtures were considered: the first one containing Fe^{3+}, Cu^{2+}, V^{5+} (M1); the second one containing Fe^{3+}, Mn^{2+}, Pb^{2+}, Cr^{3+} (M2); the third one containing all the selected metal cations, Fe^{3+}, Cu^{2+}, Mn^{2+}, Pb^{2+}, Cr^{3+}, V^{5+} (M3). In addition to the preparation of these mixtures, PM 2.5 extracted from Milan air sampling filters [17-18] was also included in the experimentation.

Specifically, the tests were carried out on samples of white Carrara marble (for a total of 88), purchased from Marmo Ornamento srl by Alberto Giananti (Carrara, Italy). Hall treated with graphitic carbon, which simulates the elemental carbon present in atmospheric particulate matter, and solutions containing the selected metal cations. These samples were also compared with untreated samples.

In particular, in order to better simulate the real aging process but in a relatively short time, the use of a chamber for corrosion tests (Fig. 1) in a humid atmosphere (introduction of SO_2) was envisaged, in line with what has been studied in the literature [19-25]. In addition, the simulation of the sunlight irradiation conducted in a special chamber (equipped with three xenon lamps) is of particular importance in the exposure cycle (Fig. 1). In fact, the increase in the temperature of the materials, which normally occurs in real situations due to exposure to daylight, could affect the catalytic mechanism of some metal cations according to the renowned Arrhenius equation [26]. Both the climate chambers were available at Innovhub Stazioni Sperimentali per l'Industria S.r.l. (Milano, Italy). To the best of our knowledge, this experimental combination turns out to be innovative as it has never been used before.

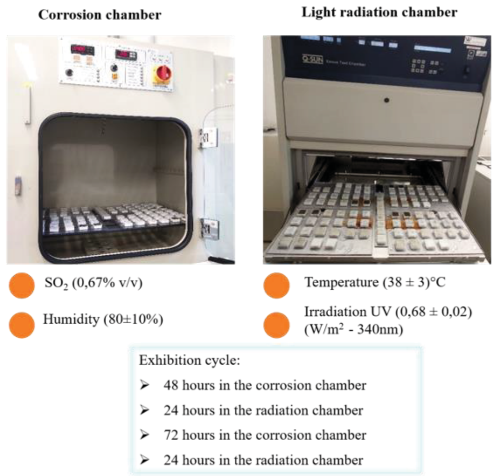

Fig. 1. Corrosion chamber, Light radiation chamber and exhibition cycles in the two climatic chambers.

The accelerated aging cycles required the marble samples to enter the corrosion chamber for 48 hours, then the samples were transferred to the irradiation chamber for 24 hours, followed by another 12-hour cycle in the corrosion chamber and finally 24 hours in the irradiation one. The 22 samples were exposed for a total of four weeks (11 samples treated with the solutions containing the cations in duplicate). 2 cycles in a wet corrosion chamber were planned for each week, interspersed with 2 cycles in the sunlight chamber (Fig. 1) in order to verify the formation of gypsum on the surface.

The physicochemical characterization of the different specimens was performed both in the pre-exposure and post-exposure phase through different analytical methods such as: colorimetric analysis, stereomicroscopic observations, SEM-EDX analysis (Scanning Electron Microscopy coupled to Energy Dispersive X-Ray Spectroscopy), IC analysis (Ion chromatography), analysis by XRPD (X-ray powder diffraction).

- 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 whit 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.

Figure 2 shows the untreated (a) and treated with PM2.5 samples before exposure (b). Samples with PM2.5 taken during the 4 weeks of exposure in climatic chambers (c-f).

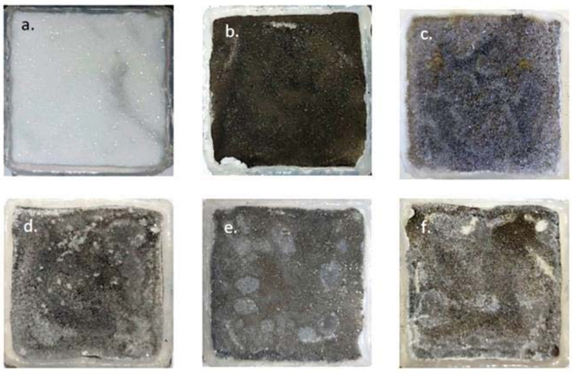

Fig. 2. Samples untreated and treated with PM 2.5 before exposure (a and b). Samples with PM2.5 taken during the 4 weeks of exposure in climatic chambers (c,d,e and f).

III. RESULTS AND DISCUSSIONS

The results obtained using a stereomicroscope (Fig. 3) showed that almost all of the samples displayed an abundant formation of gypsum crystals on the surface from the first week. In particular, the samples for which this phenomenon is more evident are those treated with M3 (mixture containing all the selected metal ions) and especially PM 2.5, compared to those treated with other metal cations and those not treated. In the second week of sampling there are no detectable differences from the first one, with the exception of the specimen treated with Pb^{2+} which shows a larger formation of gypsum crystals, suggesting a delayed catalytic activation compared to the others. In the third week, the samples develop small variations in the formation of gypsum compared to the other weeks; in fact, the formation of compacted acicular crystals is observed that originate concretions scattered heterogeneously on the analysed surface. These concretions develop on almost all the samples taken in the fourth week (some have more concretions than the others).

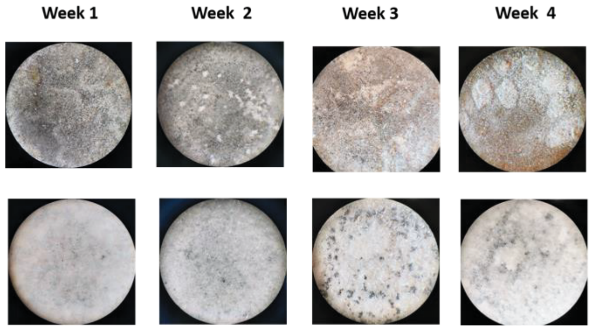

Fig. 3. Samples treated with PM 2.5 and M3 (mixture composed of all the selected metals) taken during the four weeks of exposure in climatic chambers.

The observations obtained by this method allow us to hypothesize that some metal cations act more on the initial sulphation than others, which are probably activated only later. Furthermore, it is evident that, during the fourth week, the degradation process reaches a more advanced stage.

The observations performed by SEM-EDX allowed to characterize the morphology of the gypsum crystals that evolves from a prismatic to a lamellar acicular form (Fig. 4). In addition, an increase in the thickness of the crystals was observed over the four weeks.

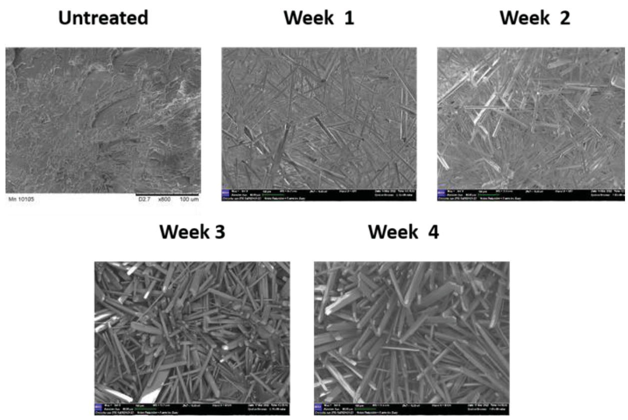

Fig. 4. Morphological images (SEM) of the gypsum crystals observed on the surface during the 4-week exposure of a type of sample.

On the samples, pre- and post-exposure, the colorimetric analysis was carried out to uniquely quantify the colour difference, as a possible objective indicator with respect to the formation of gypsum.

The colorimetric analysis, in terms of the variation of ΔL*(increase in brightness), showed an increase in this coordinate, probably attributable to the formation of gypsum (Fig. 5).

An increase in the ΔL * parameter was observed in all the samples in the first week, attributable to an increase in white gypsum crystals on the surface (as observed by stereomicroscope investigations) (Fig. 5).

As for the samples that showed a decrease in this parameter in the second and third week (Fig. 5), it was hypothesized that the gypsum tends to penetrate inside the carbonate substrate, leaving the graphitic carbon on the exposed surface that is not incorporated into the crystal matrix. In fact, it is possible to observe in some studies [27-29] carried out on real samples, that the carbonaceous particles can also be deposited on the surface. From the fourth week, the slightly increasing values of ΔL * would indicate the formation of further crystals of gypsum. This finding is confirmed by stereomicroscopic observations: in fact, especially in the fourth week, compact stratified concretions of white gypsum crystals were noted on the surface of all the samples.

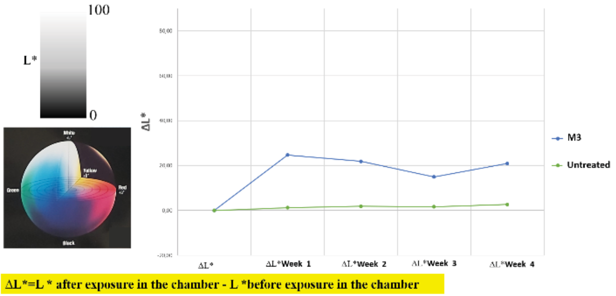

*Fig. 5. Diagram of the ΔL * values of the M3 samples compared with an untreated sample exposed under the same conditions.*

From the observation of the data obtained by ionic analysis of the anions it has been seen that all the specimens already reveal high values of sulphates from the first week. This seems to suggest that the various metals used, individually or in a mixture, early activate the formation of gypsum on the surface. An increase in the concentrations of sulphate ions was observed in the final weeks of testing for some samples (Pb^{2+}, Cu^{2+} and Cr^{3+}), suggesting that the catalytic effect for these metal cations may last over time. On the contrary, other samples showed a decrease in the concentrations of sulphate ions in the final weeks of experimentation (M2 and M3). This later result suggests that the plaster might have penetrated inside the substrate. This observation could be confirmed by stratigraphic sectional analysis using an optical microscope.

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 (Fig. 6).

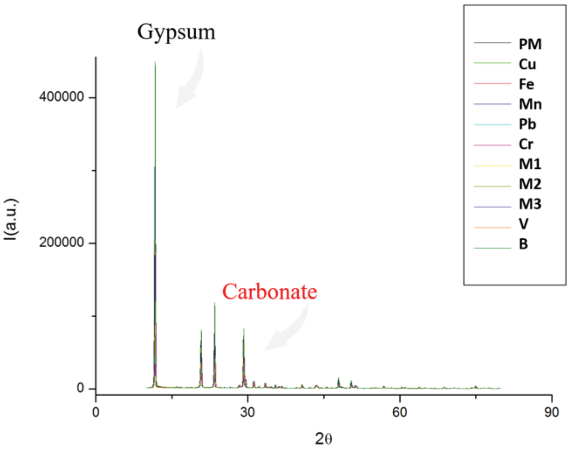

Fig. 6. XRPD patterns of the samples taken at the end of the 4 weeks.

This result confirms, for all samples, the presence of gypsum formed on the surface following chamber exposure. The presence of calcium carbonate, on the other hand, can be attributed to the involuntary partial removal of the substrate, or to the presence of calcite crystals, as they are non-cohesive for advanced degradation (Bonazza et al. 2005).

IV. CONCLUSIONS

This first phase of the experimentation has highlighted the complexity of sulphation process. In fact, there is currently no univocal evidence on the role of the catalysts in this process in relation to the results obtained, even if some conclusive considerations from this initial study can be drawn.

Some metal cations were able to activate the catalytic process faster than others. The different combinations of metal mixtures show a synergistic action that is larger in terms of gypsum formation (mainly in the following weeks in the climatic chamber).

Further tests are underway (exposure in the same chambers with lower SO_2 concentrations) which will be fundamental to fully understand this phenomenon and the role of the individual cations.

This research is essential since the experimental data will serve to create a mathematical model able to predict sulphation and therefore the formation of black crusts for a given site in relation to the atmospheric pollution that distinguishes it.

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