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EXPERIMENTS IN ACCELERATED AGEING CHAMBERS TO UNDERSTAND THE SULPHATION PROCESS

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1. 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. In this context, the present research work involved the exposure of Carrara marble samples treated with metal cation solutions in climatic 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 [1]. 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 SO_2 concentration twenty-fold lower than the first one). The aim was to better discriminate the catalytic role of individual metals.Herein we report the novel results from the second exposure campaign. This research work is part of a broader interdepartmental project of the University of Milan, entitled SciCult.

2. Results and Discussion

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 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. 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. 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). 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 (Cu2+ and Cr3+), 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 [1]. Under these new experimental conditions, the Fe3+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.

3. Conclusions

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 enablingthe 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 [1]. 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.

References

[1] V.Comite, A.Bergomi, C.Della Pina, C. Castellano, M. Borelli, C.A.Lombardi, M. Formenti, M.F.La Russa, C.Cavaterra, P. Fermo “Climatic chamber tests to evaluate the catalytic action of heavy metals in the sulphation process” (2022) 2022 IMEKO TC-4 International Conference on Metrology for Archaeology and Cultural Heritage, MetroArchaeo 2022, pp. 294-299.