Study of the catalytic action of heavy metals in the sulphation process through experimental tests in climatic chambers

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Research conducted on the degradation of cultural and architectural heritage caused by the deposition of air pollutants indicates that both sulfur dioxide and particulate matter produced by the combustion of fossil fuels are the main agents responsible for the deterioration of carbonate materials (marble, limestone, etc.). The main chemical degradation process is the sulphation of the substrate and 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 dark heterogenous encrustations known as 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. Despite the presence of numerous studies related to black crusts formation, a specific role of the single metals is still unclear. Aiming to unveil the catalytic action of different metals, a series of experimental tests was carried out in specific climatic chambers for accelerated aging.

Accordingly, several Carrara marble specimens were prepared for exposure in the chambers by treatment with particulate matter, metal ion solutions, or mixtures of metal ion solutions. Graphitic carbon was also added into the samples (except for the ones covered with particulate matter) to simulate the behaviour of elemental carbon present in polluted outdoor environments. The simulation of the aging process was carried out with the use of ~~a~~ two climatic chambers for corrosion tests in a humid atmosphere with sulphur dioxide and exposure cycles simulating solar irradiation (xenon arc climatic chamber). The exposure of the specimens was performed for four consecutive weeks and, after each week, a portion of the samples was retrieved for analysis. The chemical characterisation was carried out before and after the accelerated aging tests by means of a multi-analytical approach involving different techniques. Colorimetric analysis was used to evaluate the variation of the chromatic coordinate L (brightness), which is related to the formation of gypsum on the surface. Scanning Electron Microscopy coupled with Energy Dispersive X-ray spectroscopy (SEM-EDX) was employed to study the elemental composition and morphology of the surface and degradation products. Moreover, X-Ray Diffraction (XDR) was used to identify the mineralogical composition of the degradation layer and Ion Chromatography (IC) was performed to identify and quantify soluble salts, with particular focus on the sulphate ions. Finally, Thermogravimetric Analysis (TGA) was carried out to quantify the amount of gypsum formed, along with organic and elemental carbon present in the black crusts.

All the experimental data collected will be processed in the next stage of the project to create a predictive mathematical model. This will help predict the formation of black crusts on carbonate surfaces based on the outdoor pollution present in a given site. In fact, this research work is part of the interdepartmental SEED 2019 project of the University of Milan entitled SciCult (mathematical modelling and Scientific analysis for Cultural heritage: prediction and prevention of chemical and mechanical degradation of monumental stones in outdoor environments).