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Multiscale study of interactions between the corrosion product layer formed on heritage copper objects and organic protection treatments

Maëva L'HERONDE^{1,2}, Muriel BOUTTEMY², Delphine NEFF¹, Florence MERCIER-BION¹, Emilande APCHAIN¹, Arnaud ETCHEBERRY², Philippe DILLMANN¹

¹ LAPA-IRAMAT, NIMBE, CEA, CNRS, Université Paris-Saclay, CEA Saclay, 91191 Gif-sur-Yvette France.

² Institut Lavoisier de Versailles (ILV), Université de Versailles Saint-Quentin-en-Yvelines, Université Paris-Saclay, 45 avenue des États-Unis, 78035 Versailles, France.

In the outdoor environment, bronze and copper statues undergo alterations caused by water and atmospheric pollution. This leads to physical and aesthetic modifications of the copper objects by the formation of a corrosion product layer (CPL) composed of a thin inner layer of cuprite Cu_2O (5 to 10 μm) at the metal/CPC interface and an outer and thicker layer (20 to 50 μm) consisting mainly of brochantite $\text{Cu}_4\text{SO}_4(\text{OH})_6$. To limit these effects, the restorers mainly use treatments with microcrystalline waxes but requiring frequent applications. The search for new corrosion inhibiting treatments, non-toxic, is a major issue in the field of heritage. The new treatments based on carboxylate, saturated carbonaceous long chain, in solutions (HC_{10}) have been developed, in particular on ferrous alloys, and seem promising for copper alloys. However, little information exists on the CPC/carboxylate layer interaction mechanisms.

Our work focuses on the study of the efficiency of the HC_{10} treatment by visualizing its penetration deep inside the CPL to enhance the protection effect as well as the interactions at the CPL/metal interface from micrometric to nanometric scale via a set of complementary analytical techniques mainly implemented on cross sections: μ -Raman spectroscopy for structural analyzes, EDS and electron spectroscopies, and particularly nano-Auger, for chemical investigations. This methodology will be detailed and illustrated on samples issued from the roof of the cathedral of Metz with and without HC_{10} treatment. Main result shows that CuC_{10} can precipitate at the cuprite/brochantite interface.