Influence of subcritical treatment on the transformation and stabilization of copper corrosion products in an archaeological environment

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Abstract:
The protection and conservation of artefacts of cultural heritage (archaeological, museum, monuments, statuary ...) are a major societal stake. These are affected by interactions with the environment. This is particularly the case for metals (iron - steel, brass - bronzes, lead, etc) that corrode. This alteration can take place as soon as they are abandoned but also when they are exposed to the public. The implementation of effective restoration and protection treatments is therefore crucial. The purpose of this work is to study the dechlorination of cuprous archaeological objects by the process of subcritical stabilization. Subcritical treatment makes it possible to extract accumulated salts, especially chlorides, on the surface of the artefact during burial in different media (soil, freshwater, brackish water or sea water). Thus, the stabilization of archaeological artefacts is accelerated by this type of treatment. The technique consists of immersing an archaeological arte fact in a pressurized and heated alkaline solution. The objective is to transform the corrosion phases of copper in our case into more stable compounds without disturbing the integrity of the layer. According to the literature, the copper corrosion products frequently found are, depending on the corrosion environment, malachite (Cu_2CO_3 $(OH)_2$), atacamite ($Cu_2Cl(OH)_3$, cuprite (Cu_2O), nantokite (CuCl), chalcocite (Cu_2S), covellite(Cus) and chalcopyrite ($CuFeS_2$). In the present work the evolution of these representative phases during a subcritical treatment was tested. These compounds were ordered as commercial powder, except chalcopyrite in its natural mineral form, and atacamite and brochantite, which were synthesized in the laboratory. In order to validate and develop this process of dechlorination, subcritical treatment has been applied to these cuprous compounds. To identify the chemical transformation reactions we carried out several analyzes: Scanning Electron Microscope (SEM), X-Ray diffraction and micro-Raman spectroscopy were used to investigate compound transformations that occurred during treatments. The first results seem to show that the copper corrosion products react very quickly under such conditions and that they tend towards the formation of tenorite. However, subcritical treatment has no effect on the transformation of cuprite and sulfur copper compounds. Moreover, treatment limitations may occur from color change produced by transformations and which may impact aesthetics and physical integrity of patinas.

Keywords: Subcritical Fluid Technology, Chlorides, Corrosion, Archaeological copper alloys