

The impact of pH and temperature on copper corrosion products in subcritical conditions: delivering insight into the treatment of archaeological copper alloys

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Corrosion profiles extant on archaeological copper alloys from aerated marine contexts often comprise CuCl beneath or intermixed with a Cu₂O layer, which is normally overlaid by a range of green blue Cu₂OH₃Cl polymorphs. Depending on prevailing conditions, other chloride bearing compounds and basic copper carbonates, may also be present. Aesthetically pleasing patinas can be disrupted by post excavation hydrolysis of CuCl producing voluminous Cu₂OH₃Cl polymorphs. This can be controlled by using the inhibitor benzotriazole, except in the presence of low pH caused by hydrolysis. Alternatively, the removal of soluble chlorides (Cl⁻), using various aqueous alkaline wash solutions, offers an approach to fulfilling the aim of controlling post-excavation corrosion. Enhancing washing effectiveness by using subcritical conditions, that are claimed to aid desalination, has been experimentally studied for marine archaeological iron but has received limited attention for copper alloy desalination.

This research investigates the potential of subcritical fluid technology to release Cl⁻ and transform compounds that are commonly present on marine archaeological copper alloys. The impact of the treatment variables pH, temperature and time on analogue pressed pellets of the commonly occurring corrosion products, atacamite (CuCl₂OH₃Cl), clinoatacamite (CuCl₂OH₃Cl), malachite Cu₃(CO₃)₂(OH)₂, nantokite (CuCl) and cuprite (Cu₂O) was studied. Sets of analogues comprising 3 pellets were treated in subcritical conditions at pH8 (NaHCO₃) and pH10 (NaCO₃) for up to 480 minutes, with analysis of the concentration of Cl⁻ and pH values in the eluate at time intervals of 15, 30, 45, 60, 120 and 480 minutes. The surface and cross section of samples was analysed with SEM-EDS and ground pellet samples with XRD to detect whether transformation had occurred. To translate this into contexts for treating naturally forming corrosion product profiles, analogues were produced by corroding copper alloy coupons in a brackish environment for 12 months. Finally, real artefact samples were treated. These tests used the same subcritical methodology employed for the pressed corrosion product pellets, recording pH and Cl⁻ concentration at the same time values. Patina and corrosion layer characteristics were recorded before and after treatment using digital photography.

The outcome offered insight into the combination of variables that provided the most effective Cl⁻ extraction from Cl⁻ bearing pellets and identified transformations that would impact on colour change. Aesthetic impact was determined by the appearance of the coupons and real artefact samples pre and post treatment. This indicated that the change caused by the most effective parameters for Cl⁻ extraction would likely be unacceptable in any practical context for archaeological objects.