

Mechanistic studies of corrosion product flaking on copper and copper-based alloys in marine environments

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Abstract

Copper in its pure or alloyed state forms a large group of important construction materials for outdoor applications. This study comprises field and laboratory findings to assess atmospheric corrosion processes of bare copper sheet and three commercial copper-based alloys (bronze, Cu4Sn; brass, Cu15Zn; gold, Cu 5Zn 5Al) in chloride rich environments. Focused laboratory investigations have been conducted to assess the mechanism behind severe corrosion product flaking observed on copper and bronze at marine field conditions, an effect significantly less evident or non-existing for the brass and gold alloys during unsheltered exposures for periods up to 3 years. At present significant knowledge exists in the scientific literature on patina formation on copper at marine conditions and to some extent also for some of the alloys in chloride rich environments. However, the underlying mechanism behind corrosion product flaking of these materials at these conditions is scarcely investigated and the importance of chlorides and alloying elements not elucidated.

The starting point for this study was the identification of nantokite (CuCl) to different extent within the patina of the field exposed copper and copper-based alloys, and the well-documented ability of nantokite, trapped within the patina of restored ancient bronzes, to increase in volume in contact with humid air forming paratacamite (Cu₂(OH)₃Cl) with patina flaking as a consequence (bronze disease).

The importance of nantokite and other corrosion products formed within the patina of copper and the copper-based alloys on the extent of corrosion product flaking has been investigated via well-controlled successive cyclic wet/dry laboratory exposures in a climatic chamber and pre-

deposited quantities of chlorides. Studies with synthetic nantokite grown on copper and its transformation to e.g. paratacamite at given conditions have been conducted in parallel. The importance of humidity and chlorides on the corrosion product composition, morphology and degree of flaking have been investigated for bare copper and the different alloys via in-situ IRAS (Infrared Reflection Absorption Spectroscopy) measurements, ex-situ SEM/EDS (Scanning electron microscopy/ Energy dispersive X-ray analysis) analysis and GIXRD (Grazing incidence X-ray diffraction) examination.

Initially formed nantokite in chloride environments easily transforms to paratacamite that result in an expanded volume within the patina and severe flaking of corrosion products for copper and bronze. A rapid formation of Zn/Zn-Al chloride-rich corrosion products and the formation of more stable corrosion products within the patina of the brass and gold alloys compared with copper and bronze reduce the extent and ability of dissolved cuprous ions and chloride ions to form CuCl, and thereby the extent of flaking. The extent of flaking decreases with increasing distance from the coastal line, i.e. reduced chloride deposition quantities.

References:

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