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Fountain Encrustations and Their Influence in Protection of the Bronze Underneath

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Abstract

Bronzes of artistic fountains are frequently interested by precipitation and accretion of calcareous sediments; chemical-physical parameters of carbonate layers were measured on two monuments, mainly with a non-destructive testing – the Eddy Current methodology - and their influence on the protection of the underlying metal was inquired. The corrosion rate (c.r.) was found to depend on solution and solid phases characteristics - E_H(V) and pH of water in contact with the metal surface - and on thickness of the sediment layer: the sheltering action of a thin, compact, thight encrustation was found fundamental in decreasing the c.r..

Introduction, Materials & Methods, Results

Calcareous sediments on fountain bronze elements are, at the beginning, thin and compact, and continue growing until two situations are reached: (1) Crevices build-up and flakes detach; (2) Porosity and cracks increase causing water penetration. This was documented by SEM/EDS [1] on thick layers, but also by the Eddy Current Procedure on thin, medium encrustations, measuring the thickness on two fountains: (i) before and after accretion in successive steps, (ii) before and after cleaning the surface.

Table 1: Roma, Fountain of the Tortoises. Efebo. Evolution in time of the encrustations. Average thickness in µm. Standard deviation in brackets in µm, irregularity index underlined and computed as the ratio standard deviation/ average thickness.

Area	Time 0	After 9 months	After 19 months	After 22 months
Clean and protected surfaces				
Left cheek	69.0 (±11.5) 0.17	207.4 (±156.0) 0.75	93.7 (±38.7) 0.41	82.6 (±45.5) 0.55
Right cheek	98.0 (±17.4) 0.18	109.8 (±21.6) 0.20	115.6 (±19.7) 0.17	114.4 (±20.6) 0.25
Groin	58.0 (±13.6) 0.23	74.3 (±11.9) 0.16	91.4 (±20.6) 0.22	80.8 (±20.6) 0.25
Inner left thigh	78.0 (±18.0) 0.23	89.5 (±21.4) 0.24	82.5 (±23.7) 0.29	78.0 (±23.6) 0.30
Left knee	72.0 (±10.3) 0.14	74.6 (±10.5) 0.14	93.9 (±24.3) 0.26	76.0 (±22.8) 0.30
Clean surfaces				
Left wrist, lower part	45.5 (±15.4) 0.34	62.9 (±13.4) 0.21	89.2 (±41.4) 0.46	94.4 (±38.8) 0.41
Untreated surfaces				
Chest	570 (±113.5) 0.20	592.3 (±117.2) 0.20	688.7 (±211.1) 0.30	689.4 (±178.3) 0.26
Left calf	78.0 (±10.8) 0.14	122.2 (±28.0) 0.23	126.0 (±26.0) 0.21	107.2 (±33.2) 0.31

An example of thickness data of the fountain of the Tortoises in Roma is reported in table 1. Measurements have been extended to the fountain of the Neptune in Bologna. It is important, to judge the sheltering effect developed by the encrustations, which influences the micro-environment in contact with the metal, to take in account: (i) the correlation between E_H(V) and pH, which establishes the stability of the different electrochemical phases of copper compounds in equilibrium, and the crystallization of Cuprite; (ii) the compactness of the carbonate layer. The first condition is satisfied by a saturated alkaline solution of calcium carbonate, covering the metal [2]. The second condition is reached by a thin, regular, compact, calcareous layer, insulating the alloy. This layer, increasing the thickness, becomes porous and fragile, losing its sheltering effect [1]. The Pourbaix diagram is shown (Fig.1): the stable phase is the Cuprite in the alkaline environment [3, 4]. For a better comprehension of the phenomenon, a survey of ISCR was carried out, with the aim of measuring the rate of corrosion (c.r.) with the Rp – Resistance of polarization – methodology in different areas of the Tortoises fountain. Results [5] confirm the inverse correlation between c.r. and thickness of the encrustations.

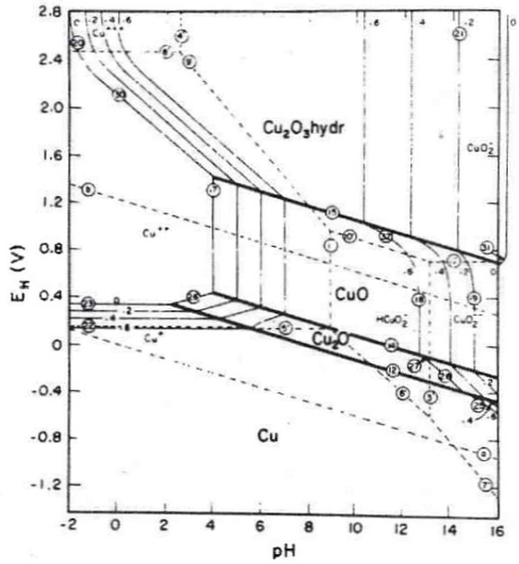

Fig. 0: E_H(V)/pH or Pourbaix diagram showing the stable phases of copper compounds, under equilibrium condition [3].

Conclusions

Research outcomes allow the following general conclusions:

This study enhances the protective role of the thin carbonate layer.

The barrier effect of this carbonate layer applies for thin encrustations; thicker layers develop to irregular structures characterized by flaking, porosity and fractures and are not protective anymore.

This research will proceed on a different monumental study site and on restored bronzes as well as on a model in the laboratory, using also water saturated by calcium carbonate as contact liquid for corrosion rate measurements with the Rp methodology.

Currently the best advice for water-softening plant guards is to keep the Langelier index slightly negative in order to avoid the covering of the bronze by a white veil, but contemporarily program periodic inversions of this index to take advantage of the alkaline barrier effect of the carbonate. Such conditions are favorable to conservation of the other component of fountains, stone.

Areas not protected by the carbonate layer are exposed to the action of chlorides and other ions acting as depolarizers and promoters of electrochemical corrosion; therefore a specific procedure for protection and corrosion inhibition is required.

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