

DEGRADATION WORKS OF MONUMENTAL ART CAST BRONZE UNDER THE INFLUENCE OF ENVIRONMENTAL FACTORS

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***Abstract:** Intensive pollution, combined with the lack of conservation of monuments exposed to these environments make the main cause of deterioration of cultural objects to atmospheric corrosion metal. This paper proposes a study of the main factors leading to degradation Bronze alloy, cast bronze monuments exposed to open atmosphere: corrosive environmental factors, stability and products of corrosion of bronze. In general, all corrosion products present on a metal surface are indicated as 'skate', can be composed of single-layer or multilayer products. The paper also includes a case study on the influence of environmental factors on degradation Matthias monument statue in Cluj-Napoca, Romania. Visual inspection of the monument informs us that have white spots, gray, reddish not consistent with the base color green patina, surfaces showing depigmentation, the rain washed areas, crystallization, deposition of air-borne particles.*

Keywords: bronze monuments, atmospheric corrosion, corrosion products.

1. Introduction

Metals are a group of highly resistant materials to environmental factors, however almost all are subject to erosion and corrosion. This phenomenon is due to a series of chemical and electrochemical reactions, depending on the nature of the metal and the conditions under which it is exposed. According to them, may be slow or rapid degradation. Copper is the most important artistic metal metallurgy both its availability and its properties of strength, malleability, resistance to atmosphere and quality alloys: bronze and brass. Copper alloys (brass, bronze) shows moderate stability under atmospheric conditions. However due to increased pollution and acid rain, urban environments exposed bronze undergoes an acceleration of corrosion and hence a depreciation of appearance. Degradation are cast bronzes of monumental artwork is a complex phenomenon and involves a certain electrochemical reactions caused by several factors such as: the nature of air pollution, metal material composition, microstructure metallic material, moisture, degree of processing surface temperature and exposure time for the development of corrosion products. This was mainly due to the interaction of water and corrosive substances from the surface [1, 2, 3].

A bronze surface exposed to the atmosphere forming a thin layer of corrosion product layer formed naturally is called patina noble [4, 5]. Final quality of the shoe varies depending on the alloy composition and environmental conditions. Chemically speaking, the layer can be described as a hydrated copper oxide stabilized copper oxide substrate. Many factors influence the initial development of the patina, some of them can be active throughout the entire existence of works of art. The most important original patina protective harmful substances are chlorine (sodium chloride, allowing the development of copper chloride), sulfates and oxides, particularly sulfur dioxide [6]. A common method to protect the bronze surface is to cover them with an artificial patina through use of chemical reagents or electrochemical methods [7, 8]. Artificial skating surface provides corrosion protection and also has an aesthetic value. The first evidence of the use of artificial patina of antiquity dating. Dating mirrors bronze age have been discovered in China, which indicated that there are chemicals deliberately placed bronze surface [8]. Therefore, finding methods of forming artificial patina to protect works of art made of bronze is a current concern.

2. Corrosive environmental factors

2.1. Influence of gaseous pollutants.

Atmospheric corrosion, even in a closed room is determined by the presence of humidity and aggressive gases (carbon dioxide, sulfur dioxide, ammonia, etc.), which are polluted atmosphere in large enough quantities. It is well known that in terms of corrosion, it is a natural phenomenon that can not be stopped was founded by the laws of thermodynamics, metallurgy called reverse [9]. In general, corrosion cells are very small, numerous and randomly distributed on the metal surface. Pollutants are specific factors involved in corrosion chemical nature and concentration of gaseous compounds, the rate of deposition and water solubility, chemical reactivity, pH. The main gases are pollutants: SO_2 , SO_3 , H_2S , NH_3 , NO_2 , CO , CO_2 and other minor organic products. Corrosion rate of copper increases when the atmosphere is polluted with high levels of SO_2 , according to the study [10], above the 0.62 to 0.68 $\text{mg SO}_3/\text{dm}^2$ copper corrosion rate increases significantly with the degree of pollution. Aqueous layer on the surface of monuments is a suitable environment for the adsorption and oxidation of sulfur dioxide (SO_2) forming a layer rich in sulfur acid. Under these conditions Cu^+ oxidizes Cu^{2+} the leading eventually to the emergence of the layer of patina on copper salts (brochantite). Synergistic effects of mixtures of pollutants have been demonstrated by laboratory tests (Figure 1), where the individual and combined effects of corrosion can be simulated and controlled [11, 12, 13, 14].

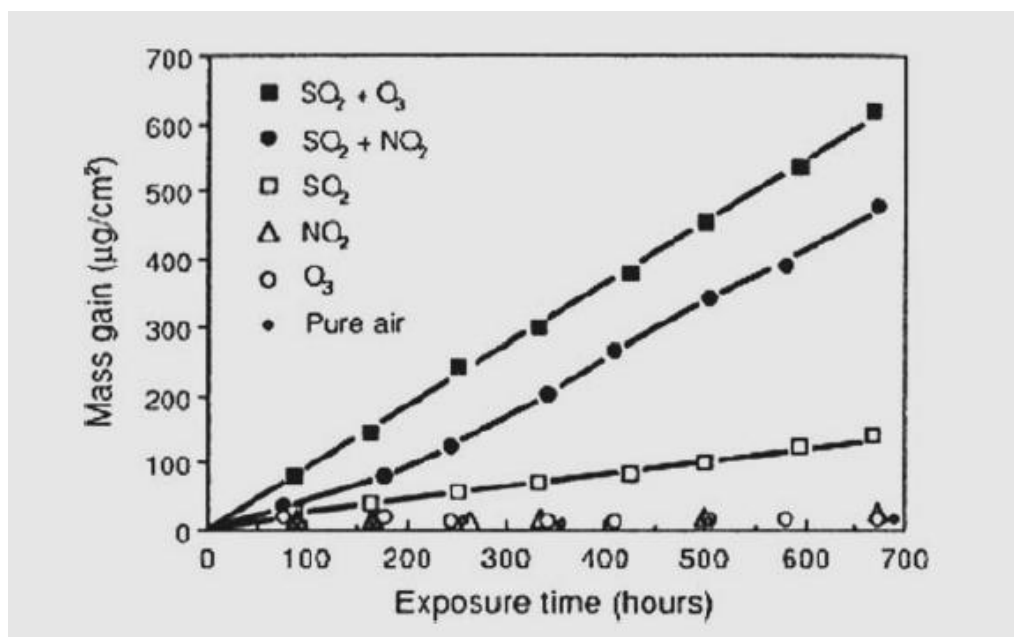


Fig.1. Mass gain of zinc samples exposed in air at 95% RH [18].

Another important factor for increasing the sensitivity of a metal in a given atmosphere is gaseous pollutant deposition velocity, defined as the ratio of gas to deposit rate metal surface and its concentration in the atmosphere [15]. (Table 1).

Table 1. Solubility and deposition velocity for atmospheric pollutants [15].

Pollutant	H [*] (mol L ⁻¹ atm ⁻¹)	Deposition velocity [†] (cm s ⁻¹)	
		Outdoor	Indoor
H ₂ S	0.10	0.38	0.03
SO ₂	1.2	0.01-1.2	0.05
NO ₂	0.007	0.02-0.8	0.006
O ₃	0.012	0.05-1	0.036
HNO ₃	2.1 x 10 ⁵	0.1-30	0.07

* Henry's law constant

2.2. Effect of relative humidity and temperature

Corrosion is an electrochemical process that requires the presence of an electrolyte due to take place. Therefore the presence of moisture on the surface of bronze leads to accelerating the patina layer formation. Several studies [10, 16, 17] have shown that in addition to other climatic parameters, humidity, the presence of corrosive species plays a major role in the degradation bronze surfaces exposed to the atmosphere. In dry oxidized copper surface to form a protective layer of Cu₂O, while the presence of a layer of water, degrade its protective nature. Some studies relate to temperature and relative humidity rate of corrosion of metals [18-21].

Figure 2 shows the evolution of corrosion depending on relative humidity and temperature environment polluted with SO₂. While corrosion increases relative humidity, temperature has a different effect: annual temperatures below 10° C, corrosion increases with temperature and this may be related to the increased humidity 80% RH > while temperatures above 0° C. Portion corrosion decrease above 10° C on the graph is assigned a higher speed evaporation of moisture layers after periods of rain or dew and a surface temperature higher than the ambient temperature due to solar radiation which leads to a decrease maintenance time surface moisture [22].

2.3. Other influences

Chloride ions also have a strong influence on the atmospheric corrosion of copper. Some studies [10] show that the level of pollution of the order 300 to 600 mg NaCl/m² causes a marked increase in corrosion for pure copper.

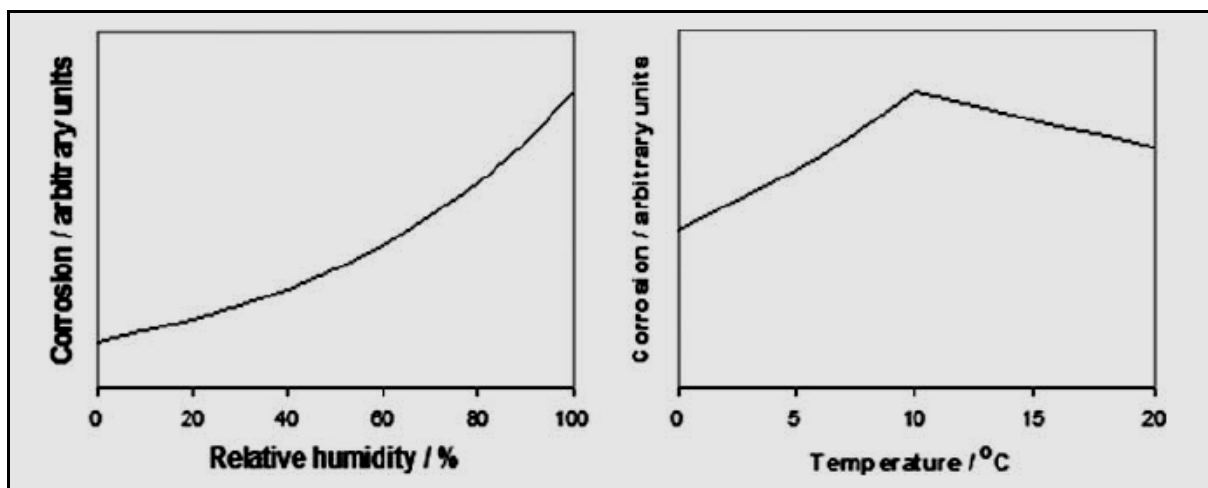


Fig.2. Effects of the relative humidity (left) and the temperature (right) on metal corrosion in a SO₂ polluted environment [22].

Studies show that between corrosion rate and exposure time there is a relationship (1) of the form:

$$C=A \cdot t^n \quad (1)$$

Where A and C are corrosion loss after one year, respectively after "t" years of exposure. C / t is the corrosion rate, and A, n are constants specific "site". It was found that a sufficient amount of rainfall can mobilize soluble corrosion products on the surface leading to destabilization of an emerging patina look scum. A high porosity and surface defects facilitates multiple entry and retention corrosive species. Another factor influencing the atmospheric corrosion of copper is exposed to the atmosphere configuration object [10]. For example, a horizontal surface has a speed of corrosion, higher compared to a vertical surface also has high corrosion areas that accumulate watery due to improper drainage.

3. Stability and corrosion products of bronze

In the field of corrosion and, in general, to know the behavior of metals in aqueous solutions is called the Pourbaix diagram describing the stability of a metal exposed to a given environment as a function of: Potential - pH. These charts give a visual representation of oxidation and reduction skills to determine the major components of an element [23]. Usefulness diagram is overlapping fields E and pH parameters for which combinations are stable and water represented by blue lines (Figure 1.3) representing the decomposition of water left by the evolution of the hydrogen by reacting 1 or oxygen through reaction 2.



The two blue lines attached to an area where water is stable. For combinations with potential (2) and pH above line, water is unstable and decomposes with evolution of oxygen. The potential combinations (1) the bottom line is also unstable and decomposes with evolution of hydrogen.

Copper has a potential standard for the two lines: E° , for the redox system $\text{Cu}^{2+} / \text{Cu} = + 0.33$ V SHE, so copper is not corroded in acidic solutions without O_2 , but is damaged in acid aerated and solutions based.

Figure 3 (right side of image) shows the Pourbaix diagram of copper immersed in water. If the form CuO , copper is protected in this area is passivated. In areas where copper is in its ion is active corrosion, while copper is immune to alkaline environment (the bottom of Figure 3) [9].

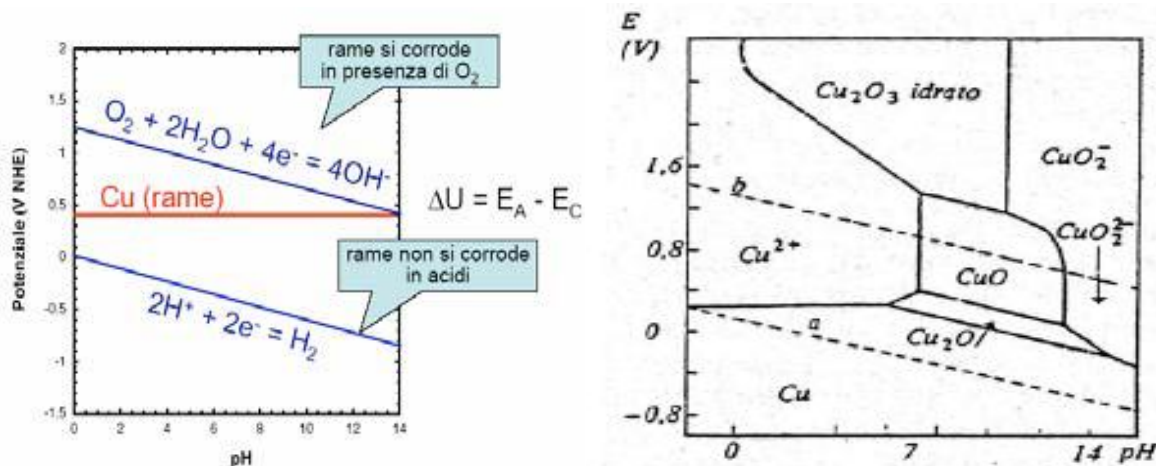


Fig.3. Pourbaix diagram of copper in water [9].

3.1. Patina

Some studies have shown general reaction schemes describing the evolution of the copper patina, due to variations in environmental pollutants, to explain the mechanism of corrosion. In the absence of corrosive gas species, a reactive metal exposed to air develops a thin layer protection, often composed of oxides or hydroxides, which reduced ionic transport properties. This creates a barrier to further corrosion. Surfaces exposed to humid air with a relative humidity criticism, a thin mono absorbs water surface. The absorption of atmospheric gas esand deposition of airborne particles in the water layer depends on surface dissolved ionic species that control electrolyte composition [24, 25]. Figure 4 shows the sequence of corrosion products formed on copper exposed to urban environment characterized by the presence of SO_2 and exposed to marine sites where the presence of sodium chloride is predominant [26].

Generally, all corrosion products present on a metal surface are indicated as „skate”, not to mention a distinction between different possible compounds, coatings and morphology. There are lots of morphologies and are important because they show different corrosion processes, different properties in different conditions patina of the metal [9]. Patina may be composed of single-layer or multilayer corrosion products. In general, it can be seen as a continuous development of products and can reach micrometer thick. Corroded surfaces encountered can be classified into two categories corrosion patterns: type I and II [17]. Both can be seen on a single artifact. Type I is flat object surface appearance is preserved, while type II or a rough surface, shape and surface are heavily damaged.

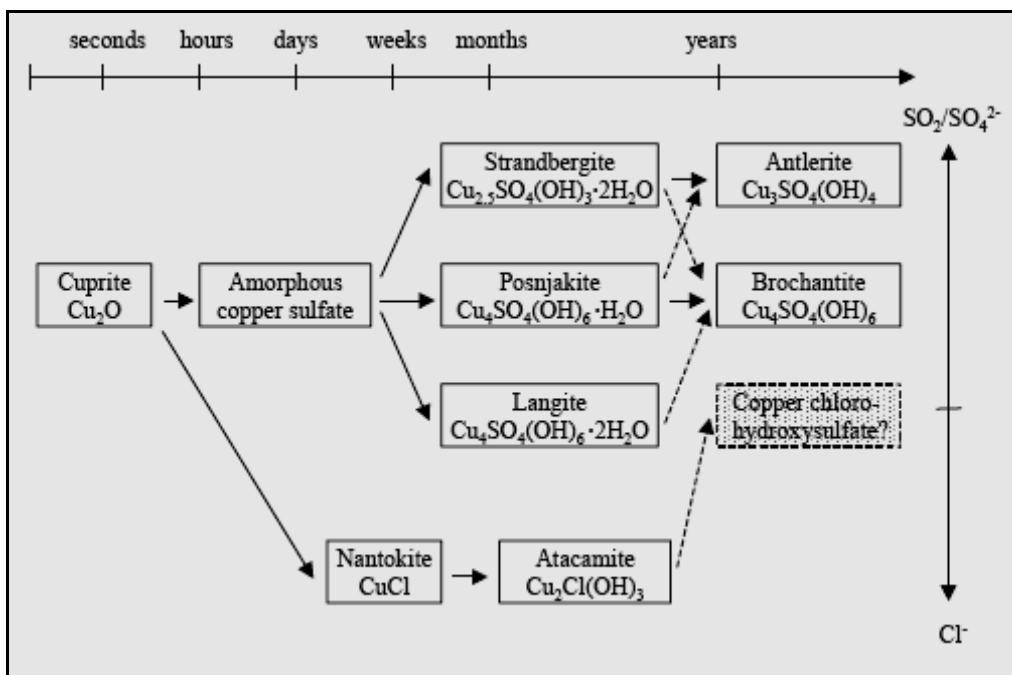


Fig. 4. A scheme for patina formation of copper exposed to sulfate or chloride environments [26].

4. Case study

Matthias statuary group, a symbol of Cluj-Napoca, Romania, was erected in the town square in 1902. The monument is exposed in a polluted atmosphere created by urban skate destabilized made while protecting the metal. Atmospheric conditions it is exposed to the monument are: SO_2 concentration - 6.58%, NO_x concentration - 36.75%, NH_3 concentration - 56.67%; pH - 5.6; average rainfall 675 mm / year. Visual inspection of the monument informs us that have white spots, gray, reddish not consistent with the base color green patina, surfaces showing depigmentation, the rain washed areas, crystallization, deposition of airborne particles. Following precipitation, alkaline substances in products of corrosion are colored limestone pedestal, indicating solubility shoe (Figure 5a and b) [27]. In Figure 6, there is partial dissolution of natural patina, porous surface water infiltration caused skate grip giving unstable and porous structure of the surface has the ability to retain compounds contamination (airborne particles). Rain protected areas appear darker due to accumulation of atmospheric products: carbon of gypsum, feldspar which were cemented to the surface in some places monument thickness 2-3 cm (Figure 6 b). Statues were identified surface accumulations of bright green mineral that is not heavily feature malachite green (Figure 7 a and b). Were studied crystals composing the crust covering statues of bronze. They have optical properties similar to Atacama, calchonatrit, brochantit or antler, and asbestos is a catalyst for reactions of sulfate and carbonate alteration minerals [28-30]. Their presence can be attributed to emissions from burning materials containing chlorine, from an attack of the surface with chemicals containing chlorine or asbestos in high-traffic urban environment. This: the presence of copper chloride has been shown experimentally from X-ray diffraction analysis (Figure 8 a and b).



a



b

Fig. 5. The King Matthias statuary group in Cluj-Napoca, Romania (a) Detail (b) [27].



a

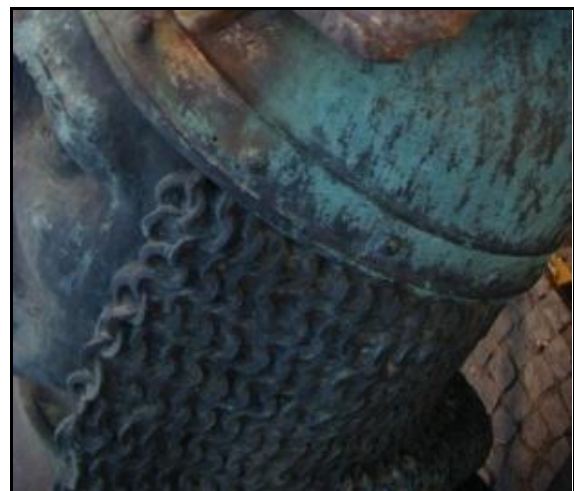


b

Fig. 6. Images illustrating the degradation of statuary Matthias (detail) [27].



a



b

Fig. 7. Images illustrating the degradation of statuary Matthias(detail) [27]

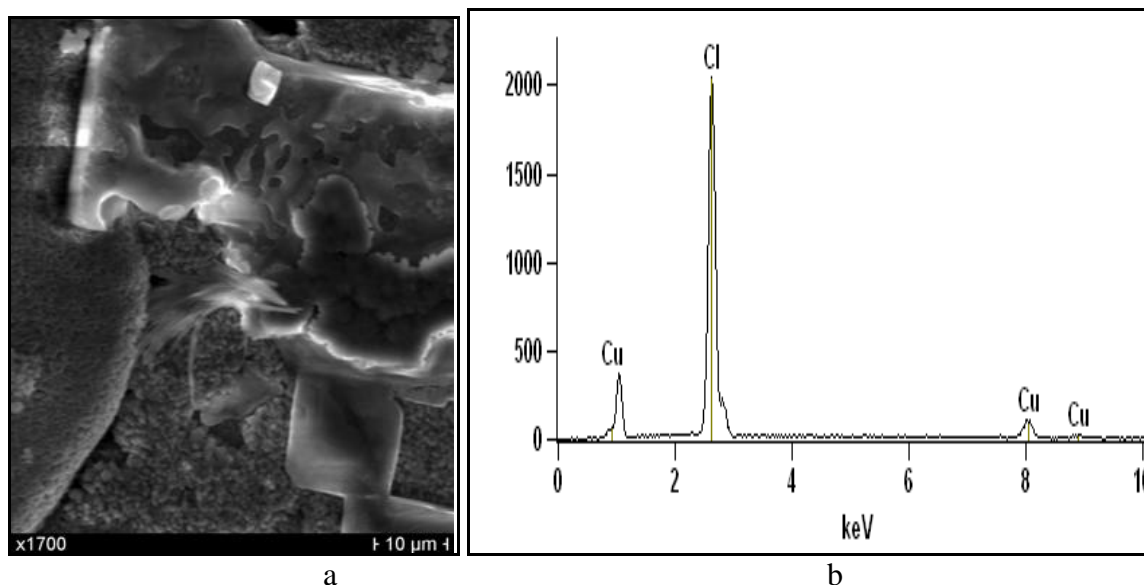


Fig. 8. SEM analysis results (Secondary Electrons images) at x1700 a) and EDS analysis of the patina [31].

Conclusions

Alloys such as brass, bronze shows moderate stability under atmospheric conditions, but due to increasing pollution and acid rain, urban environments exposed bronze undergoes an acceleration of corrosion, expressed by some impairment of appearance. Degradation of cast bronzes of monumental artwork is a complex phenomenon and involves a certain electrochemical reactions caused by several factors such as: the nature of air pollution, metal material composition, microstructure metallic material, moisture, degree of processing surface temperature and exposure time for the development of corrosion products. This was mainly due to the interaction of water and corrosive substances from the surface. Unlike usual results of corrosion, very old skates object formats are appreciated (subjectively) attractive because of their color and their association with age.

Need for corrosion protection of bronze monuments exposed to the atmosphere, made their corrosion study is a current concern. It is necessary to find solutions to protect the surface against damage bronze monuments, especially with, as they are real cultural heritage of each country.

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