

## **Conservation and restoration of the Don José I Monument in Lisbon, Portugal. Part II: Metal components**

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### **Abstract**

The equestrian statue of D. José I, in Lisbon, is a masterpiece of the sculptor Joaquim Machado de Castro. It weights over thirty eight tons and was made in a single casting by Bartolomeu da Costa in a copper alloy (brass). After over two centuries exposure, the statue presented an unappealing heterogeneous appearance and showed some deterioration features that required attention. Preliminary studies showed that the deterioration phenomena were typical of copper alloys exposed to outdoor urban environments. The proximity of the seacoast also contributed to some specific decay mechanisms. The highly contrasting patterns of the superficial patinas consisted of black dense deposits covering an original cuprite layer side by side with the common green deposits of basic copper sulfates, hydroxides and chlorides. The highly corrosive nantokite was present in sheltered areas, where chlorides are able to accumulate. The conservation intervention included cleaning, mostly carried out with low pressure jets of round glass beads. Onsite tests were made to select the cleaning levels required to match the areas of black and green patinas. A reddish brown cuprite layer was found underneath most of the areas with black dense deposits, while it could only be perceived by transparency on the green covered areas. When a high contrast remained between the two areas, these were mitigated with the application of water colors during the final protection phase. Nantokite active areas were passivated with sodium oxalate after the entire statue was first washed with clean water and treated with lime water to leave an alkaline reserve to slow down the eventual corrosion process, and the sculpture rinsed with ethanol to accelerate its drying. The final protection was made with Paraloid B44 and microcrystalline waxes.

**Keywords:** D. José I statue; copper alloy corrosion; cleaning; passivation;

## **1. Introduction**

The equestrian statue of Don José I was designed by Joaquim Machado de Castro (1731-1822) who won the competition for this monument in 1770 [1,2]. It was the first metal statue to be cast in Portugal, and it was cast in one piece by Lieutenant General of Engineering Bartolomeu da Costa, in October 1774. The casting in the lost-wax method, was carried out at the army armory, now the Military Museum, and the larger than life statue has a weight was over thirty eight tons. A thousand men were needed to move it from the armory to the Commerce Square, Praça de Comércio, and required demolishing the last medieval gate, Porta da Cruz, of Lisbon.

The statue, above an elliptical base in stone in the Commerce Square), faces south looking upon the Tagus river where it flows into the sea. On the south side of the base there is a medallion in a copper alloy with the bust of the Marquis of Pombal, Prime Minister of the King who organized the reconstruction of downtown Lisbon after the devastating earthquake of 1755. One of the interesting features of this statue is that the mounted King is riding over snakes representing his enemies. It has been noted, that fewer pigeons roost on this statue than on any other one in the city, and this has been attributed to the metal snakes twisting under the hoofs of the horse. The monument has been exposed for nearly 250 years in an urban environment in close proximity to the sea and therefore has been subjected to both a marine environment and heavy anthropogenic air pollution.

## **2. Condition of the Statue**

The equestrian statue showed a heterogeneous appearance resulting from the interaction of atmospheric pollution with the copper alloy used for the statue (Figure 1). Upon analysis of the alloy it proved to be a brass (copper-zinc alloy) rather than a bronze (copper-tin alloy) and its approximate composition is 81% copper (Cu); 14% zinc (Zn); 2.6% lead (Pb); and 2.4% tin (Sn) [3] although it could also be considered a quaternary bronze. The tin content in this alloy contributed to its good resistance to an urban-marine environment corrosion which had been compounded by intense traffic and industrial generated air pollution. The latter has diminished since the early 1990s with the closure of several chemical industries installed in the bank across the river, and recent rehabilitation works in the square have reduced the urban pollution, although a still crowded traffic road continues to cross the Square in its south side.

The main direction of rain and winds is from the SW, thus the south and west sides of the statue are subjected to more rain and wind than the north and east sides. The former, rain exposed sides show a green patina, while the latter have mainly a black patina covering them. Large areas of the statue are covered with a dense black patina, extremely adherent to the substrate. This fairly uniform patina forms alternating stripes with the underlying green patina in areas with intermittent water run-off. In others, small minuscule black islands appear in the green covered areas. The black color is mainly due to air pollution particles deposited on the surface. The spatial distribution of these patterns, their composition and stratigraphic layering have determined the approach to be followed in the intervention as discussed below (Figure 2).



Figure 1. D. José I statue in Lisbon. East view (left) shows the prevalence of dark patinas, while in the west side (right), more exposed to the marine winds and rains, green patinas prevail.

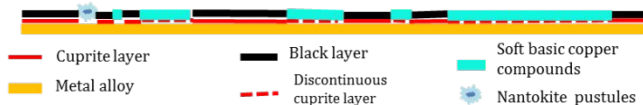
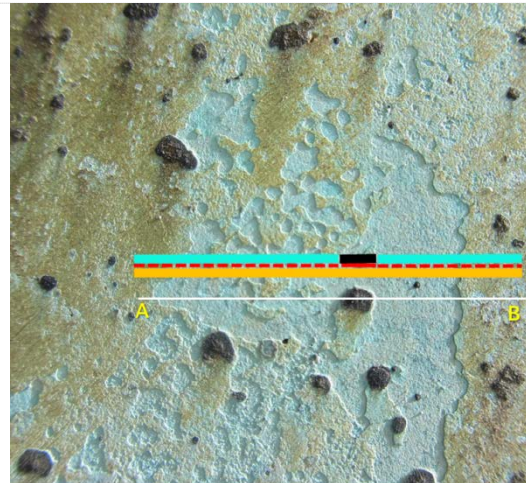


Figure 2. Sequence of black and green stripes in areas affected by intermittent runoff water (left figure-width 20 cm) and the typical green deposits where some black “islands” remain (right figure-width 5 cm). The colored bands are schematic representations of the stratigraphic sequence across lines AB in each picture. The greenish pustules in the black stripes in the left are eruptions caused by the formation of nantokite.

In sheltered areas, the green patina is covered with a blackish one, in general less adherent and softer than the black patina that exists overlaying the cuprite layer. In protected horizontal areas, such as below the belly of the horse, some brownish stains from rust are present which could have originated from iron present in air pollution.

## 2.1 Alteration of the copper alloy and stratigraphic sequence of the alteration products

In 1998, a sampling campaign of the various alteration products of the statue was carried out and a comprehensive report was prepared based on their analyses and interpretation [1]. The results obtained allowed to elaborate a model to interpret the basic sequence of the corrosion events and Figure 3 illustrates this sequence with photographs illustrating this process. Where decay is not very intense, the copper alloy has still the original cuprite layer, which is found mostly under the deep black colored patina. Cuprite, a protective cuprous oxide ( $\text{Cu}_2\text{O}$ ), is well preserved as a continuous layer below this adhering black patina, because the alteration process was not able to destroy that protective layer. In areas more exposed to the aggressive environment, the corrosion processes led to partial dissolution of this protective cuprite layer so that new copper compounds, such as sulfates, at the expense of the cuprite layer which progressively disappears. In the more exposed green areas, cuprite is present as a discontinuous layer or even absent (Figure 3). The frequent black spots dispersed along most of the green areas are residual islands of cuprite covered with the adhering black patina.

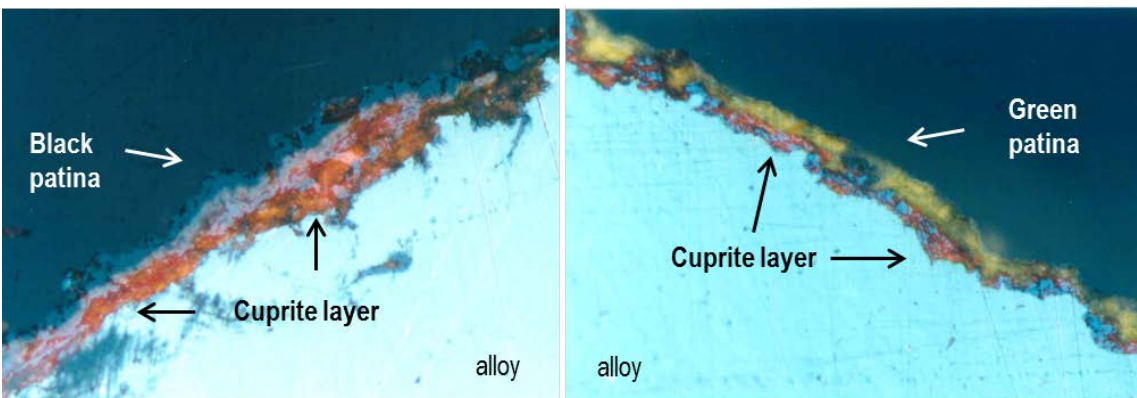


Figure 3. Microphotographs of cross sections in polarized light with Normarski interference contrast. The cuprite layer in red is more or less continuous under a dark patina (left) while it is clearly discontinuous under the green patina (right). The width of each figure is about 1.2 mm.

Figure 3 shows microphotographs of cross sections showing the two typical situations encountered: dark patinas on the left; green patinas on the right. It can be seen that under the dark patinas, there is a fairly continuous red layer, which analysis has shown to be cuprite, the cuprous oxide ( $\text{Cu}_2\text{O}$ ). Contrariwise, the green patinas, —mainly composed of brochantite, a basic copper sulfate ( $\text{Cu}_4\text{SO}_4(\text{OH})_6$ ), and mushitonite, a copper tin hydroxide ( $\text{CuSn}(\text{OH})_6$ ), — only have a discontinuous cuprite layer underneath them. The hydrated basic copper chloride ( $\text{Cu}_7\text{Cl}_4(\text{OH})_{10}\cdot n\text{H}_2\text{O}$ ), as well as a basic lead, iron copper sulfate ( $\text{Pb}(\text{Fe,Cu})_3(\text{SO}_4)_2(\text{OH})$ ) were also identified in association in the green areas not fully exposed to direct washing rains [1].

In some sheltered areas, a blackish patina occurs over a green patina with frequent presence of greenish pustules and other similar surface disruptions (Figure 4). In these areas, the superficial alteration products are constituted mainly by the hydrated basic copper chloride mentioned above, with some quartz ( $\text{SiO}_2$ ). In green areas below the black patina, a basic copper chloride

was found, atacamite ( $\text{Cu}_2(\text{OH})_3\text{Cl}$ ), as well as cuprous chloride, nantokite ( $\text{CuCl}$ ) [1, 4,]. Contrarily to the basic copper sulfates, nantokite is unstable and it doesn't offer any protective action to the copper alloy. This circumstance implied the need to address the areas with nantokite as requiring specific measures to stop or at least to drastically reduce the impact of this alteration mechanism in the overall condition state.

The brochantite formed can be attributed directly to the reaction with sulfur oxides from air pollution present in the atmosphere, while the basic copper chloride formed can be linked to the presence of chloride salts in the atmosphere due to the proximity of the seacoast [1].

The cuprite layer provides some protection to the underlying metal, while the green brochantite, despite being a fairly stable compound, does not provide the same level of protection, since in the presence of increased acidity and sulfate contaminated atmospheres it may be converted to soluble sulfates. Some of the green patinas proved to be very soft and in some cases, detached easily, while in others they still adhere strongly to the cuprite ( $\text{Cu}_2\text{O}$ ) layer. In general, corrosion is more advanced in the areas covered by green patinas than in those with black ones.



Figure 4. Aspect of the green patina covered with a blackish layer (left), and a detail of the surface pustules and disruptions (right).

A yellowish-orange colored deposit was present as a transparent veil in a quite generalized way and sometimes concentrated and more intensely colored in a few restricted and circumscribed areas. This can be attributed to the presence of iron compounds that are mostly amorphous and which are deposited from suspended air pollution particles. The oxidation of the iron armature within the statue and of other small iron elements outside it, such as core pins, can account for the iron presence in the more concentrated areas.

## 2.2 Patina development and consequences for the conservation

Following the currently accepted model for copper alloys corrosion in urban environments, the development of the identified alterations in the D. José I statue could be summarized as follows:

- i) Once installed in the Commerce Square the copper alloy (a brass that in general is considered as having better performance in marine environments) that according to oral tradition was golden when inaugurated, developed a continuous cuprite layer that offered an effective protection to the statue for many years;
- ii) The increasing deposition of atmospheric soot and the initial development of corrosion products covered the statue with a more or less continuous black patina. A confirmation of this can be found in the name “Black Horse square” given by English tourists [5, 6];
- iii) Currently, large areas are still directly connected to that initial corrosion condition and they constitute the best preserved areas of the statue.

Figure 5 illustrates the first steps of the progressive disruption of the original protective cuprite layer. On the left, the cuprite layer is still perceived through the relative transparent black patina while the green stripes are at a lower topographical level, as a result of the erosion of the upper cuprite+black layer. On the right, the surface during a cleaning test is shown to illustrate the presence of a continuous cuprite layer after removal of the overlying black patina, as well as several dispersed “islands” of cuprite in the prevailing green areas. Also to be noticed is the reddish colour perceived as an underlying layer seen by transparency through the green cover.

The continuity of the cuprite layer in both situations is highly contrasting, as seen in cross section (Figure 3), but also perceived in superficial shots (Figure 5, right). These differences in the cuprite layer occurrence may correspond to two different genetic stages: initially, when a continuous layer could be formed, and subsequently, when cuprite no longer could form because of changed conditions so that it only developed discontinuously and was therefore far less protecting. The occurrence at two clearly distinct topographical levels, as seen in Figure 5, may constitute a significant evidence for this process.



Figure 5. Aspects of the cuprite covered situation (coloured reddish) and its transition to the copper green compounds. Left: Cuprite is the underlying layer of the black soiling; the green stripes have formed along the water runoff paths and stay at a lower topographic level showing that erosion has already taken most of the cuprite layer. Right: During a cleaning test the black soiling was removed leaving an almost continuous cuprite layer. The green compounds encroach on the cuprite layer leaving behind some residual cuprite islands.

The passage from a stable copper alloy+cuprite+black stage soiling to the second stage of progressively more unstable phases is induced by the attack of atmospheric SO<sub>2</sub> and the chloride salts derived mainly from the sea mist. The sulfates, brochantite, mushitonite, are relatively soluble, but still offering some protection, while the cuprous chloride nantokite is highly soluble and very aggressive to the substrate. Figure 6 illustrates a transition zone between the black and green areas. In the interface with more sheltered areas, where chlorides may accumulate, the presence of nantokite in the pustules suggests that this corrosion mechanism has a relevant role in the destruction of the protective cuprite layer with its covering black deposits.



Figure 6. Aspects of a transition zone between the black and green patinas (left). The small bright dots of nantokite identified in the detail (center) show that they are in fact pustules protruding through the black cover thus acting as an entrance window of the corrosion agents to the underneath copper alloy. The same area after cleaning (right).

### 3. Conservation

The conservation approach took the above corrosion evolution model into account by exploring the benefits of positive situations and minimizing the more negative ones. Cleaning tests were made on typical black and green areas to define the cleaning levels and to select the appropriate cleaning tools. When cleaning the black areas, a continuous reddish cuprite layer was reached and this was readily accepted as a suitable cleaning level for this type of soiling. For the green areas, it was known that a continuous cuprite layer was not present and therefore a different cleaning level had to be defined. The soft green deposits did not offer a suitable protection and their removal was mandatory, however, the amount to be removed did not have a well-defined level and therefore had to be defined during the cleaning tests. Starting from a highly contrasting green patina, cleaning was pursued slowly until reaching a level where a reddish color could be perceived by transparency below the green deposits. This cleaning level was considered to be a suitable match to the neighbouring reddish cuprite layer.

Areas with nantokite pustules represented the worst scenario for conservation. The soft products had to be eliminated and the existing chloride ions removed as far as possible. To avoid a repetition of this alteration mechanism, other measures were implemented as discussed subsequently.

### 3.1 Cleaning

Cleaning was one of the major operations required for the preservation of the statue. The memory values associated with it and its current impact in the popular iconography, required that the color contrast of the sculpture should be minimized. To balance the iconographic objectives with the conservation needs constituted a major challenge for the intervention team. Loose dust and soiling concretions were eliminated with water and soft brushing. Alteration deposits and the more adherent black ones were cleaned with controlled particle jets. To remove these deposits, a micro-jet sprayer at low pressure was used to spray spherical glass particles perpendicularly to the surface to clean as well as and to improve compaction on the irregular metallic surface. The experience obtained during the cleaning tests corroborated the patina development models, however a uniform clean level could not be attained, since the surface no longer is homogeneous. In areas where highly contrasting patterns coexist side by side (Figure 7), a balanced cleaning level was quite difficult, if not impossible to achieve, and only artificial patination applied at the time of the final protection solved the problem of disfiguring colored stripes.



Figure 7. Aspect of a zone with highly a contrasting colored pattern before (left), after cleaning (center) and after cleaning and artificial patination (right).

### 3.2 Corrosion treatment

Once cleaning was completed, the whole sculpture was washed with water and left to dry. A lime-water solution was applied to the entire sculpture to leave an alkaline “reserve” to counteract the attack by the more aggressive acidic components in air pollution.

In the zones where nantokite was forming, a specific treatment was necessary since corrosion by sodium chloride is an auto propagating process because the chloride ion from the cuprite is released once this cuprous chloride is transformed in other less soluble compounds such as brochantite, other sulfates, or carbonates. The traditional process to attack this problem is the application of corrosion inhibitors, such as benzotriazole. Since most of these products are toxic



and may even be mutagenic, a different approach was followed, such as applied in the case of the copper roof of the Santa Maria delle Grazie, in Milan. In this intervention, a sodium oxalate solution (5% w/v) was used with a very positive outcome [7]. A similar approach was used on several bronze sculptures in Milan, with excellent results [8]. Therefore, this same approach was used on the “cleaned” statue of D. José I statue. The positive results can be explained by the reaction that occurs during the treatment:

nantokite ( $\text{Cu}_2\text{Cl}_2$ , *slightly soluble*) + sodium oxalate ( $\text{Na}_2\text{C}_2\text{O}_4$ , *soluble*) + oxygen ( $\text{O}_2$ , *gas*)  $\longrightarrow$  cupric oxalate, ( $\text{CuC}_2\text{O}_4$ , *green, insoluble*) + cupric oxide ( $\text{CuO}$ , *tenorite, black, insoluble*) + sodium chloride ( $\text{NaCl}$ , *soluble, eliminated by washing*).

The sodium oxalate promotes the oxidation of Cu(I) of the nantokite to Cu(II) which forms more stable and insoluble compounds that are found in naturally produced corrosion products of copper alloys exposed outdoors.

For the D. José I statue, a few test areas were treated and left under an artificially wetted environment to speed up the corrosion process. The treated areas proved to resist much better than the untreated ones, thus validating the premise of the treatment. After treatment with the lime-water and sodium oxalate, the sculpture was washed with ethanol to help eliminate any adsorbed water to ensure its removal.

The final treatment consisted of the application of several layers of protecting resins, such as Paraloid B44, and microcrystalline wax. During this phase, the areas with higher contrasting appearance were retouched with watercolor paints to achieve a more homogeneous appearance consistent with the iconographic value of this masterpiece sculpture (Figure 8).

The conservation intervention of the entire monument was carried out in a year and was completed by the end of July 2013.

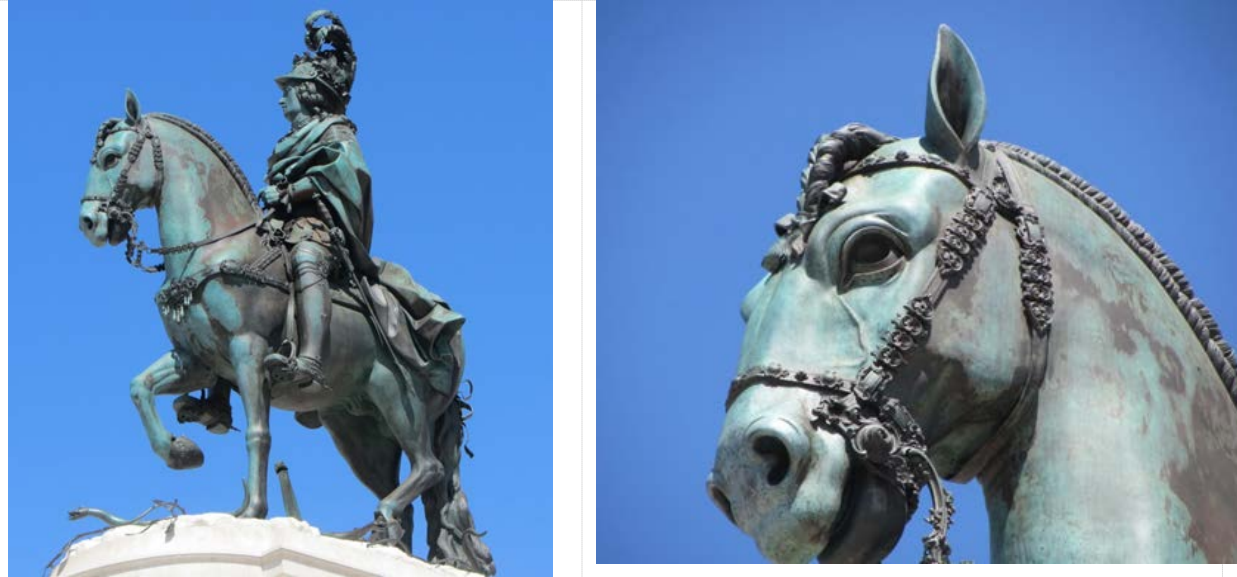


Figure 8. View of the statue after the intervention (left) and a close up detail (right).

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