Electrochemical characterisation of patina protectiveness evolution on outdoor bronze sculptures

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Abstract

A modern aesthetic criterion focuses on the visual effect produced by the original patinas colour transformations. The La Recoleta cemetery is one of the sites where numerous bronze sculptures, recognised by their aesthetic and historical value, can be found. Three works in this cemetery were selected for this study. The aim of this work was to elaborate an intervention criterion based on the present state of patinas by means of non-destructive in situ analyses. On different coloured areas the electrochemical behaviour and chemical composition of patinas were determined. Our interdisciplinary intervention policy considers the aesthetic intention of the sculptor and the transformation of the original patina since the sculpture installation to its present reading, in the frame of a scientific and historical study.

Keywords: patina, electrochemical potential, protectiveness, in situ, bronze, monuments.

1. Introduction

The public space of Buenos Aires City has numerous sculpture repositories made by European and Argentine sculptors, cemeteries among them. That of La Recoleta is recognised by its aesthetic and historical value. The selection of this material is based on its expressive potential and conceptions around temporality (Crespo, 2002). Time and its effects are part of the expectations of the authors either in the maintenance of a uniform colour or in the chromatic heterogeneity achieved since the beginning of the work and accentuated in the course of time by its outdoor exposure (Crespo, 2001).

Both reasons, taking part in the aesthetics of the sculptures are observed in the studied art works: the sculptures "El Karma", by Troiano-Troiani, the two metallic pieces of the group Mausoleum to Adolfo Alsina, by Margarita Bonnet, and “El Cristo Central” by Zonza Briano.

In the first and third, “El Karma” and “El Cristo Central” respectively, the artists intention with the artificial patina developed was to create an heterogeneity associated with

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colour (green bluish, green yellowish) emphasising the concave and convex areas in the formal interpretation of the work (Crespo et al, 2000). Conversely, in the metallic sculptures of Monument Tribute to A. Alsina, the intention was to create an homogeneous artificial green patina whose harmonic relationship with the rest of the materials (red granite stone and white marble of the exalted figure) determining the reading rhythm of the monument (Tribute commission, 1915). To define the instance in the piece time circuit during the work diagnosis, we refer to the Restoration theory of Cesari Brandi: "Time, however it may structure the rhythm, is present in the work in three moments, not yet under the formal aspect but in its phenomenology, whatever the masterpiece it concerns. First as duration of the piece while it is being conceived by the artist; secondly as the interval since the end of the creative process to the moment in which our consciousness updates the masterpiece and thirdly as the instant of the art work irruption in the consciousness" (Brandi C., 1988).

In this diagnostic work we will focus on the span of time starting from the creative process to the present moment, when the patinas transformations are altered with the purpose to establish the moment of the piece in which intervention occurs in each case.

Nevertheless it is during this exposure (by the atmospheric pollutant causing alterations) and due to the uneven quality from smelting (as far as heterogeneity of the alloy and patches made with different alloys further to the original cast) that patina transformations change from their positive chromatic and protective characteristics to a negative sense (unpleasant aspect and protectiveness decrease).

Atmospheric corrosion, the most frequent cause of destruction of different metals and alloys, has increased in the last years, especially in urban atmospheres, due to the action of different environmental polluting agents and acid rain. This type of corrosion is electrochemical and is favoured in atmospheres with high relative humidity, since the electrolyte is a liquid water layer originated from rain, dew or condensation. The magnitude of the attack depends on the time during which this water layer remains on the metallic surface and it is influenced by a series of factors like humidity, temperature, rain, solar radiation, atmospheric pollution, etc. (Arroyave et al. 1995, Oescht et al, 1997). Hence, it depends strongly on the climatic conditions where the metal is exposed (Masamitsu, 2003). Humidity, temperature and atmospheric polluting agents of a certain region constitute its "macroclimate" whereas the "microclimate" is the specific condition surrounding the object and in areas of the work, depending on the sculpture morphology. It is defined by factors like the time of wetness (TOW) of the surface or dew condensation, heating of the object by the solar radiation, hygroscope deposits and the ion accumulation of the acidic nature (SO_2^-, NO_2^-, Cl^-) of the surface water film.

When copper is exposed to natural atmospheres it begins to lose its characteristic brightness to develop a dark coloured film adhered to the base metal. It tends to turn brownish green first, then bluish green and finally green. That film is called patina, the name derived from that given by the ancient Romans to green deposit on plates of copper, bronze or brass (Almeida 1997).

The colour, morphology and texture of the patinas depend on the nature and proportion of their chemical components, which are determined by several factors. These are the compounds present in the atmospheres and their concentration, time of exposure of the sample, etc. The first corrosion product that forms on the copper based alloy surface is cuprite (Cu_2O). Later the cuprite reacts slowly with the components (O_2) and polluting agents of the atmosphere (SO_2, Cl^-, CO_2) forming alkaline salts. The copper patinas are chemical and structurally complex compounds and their components are related to the species found in the atmosphere (Graedel, 1987, Fitzgerald, 1998, Strandberg, 1998). The more common products are the copper oxides (CuO and Cu_2O) and the alkaline copper sulphates, carbonates and chlorides, all of them very insoluble water compounds. These patinas are heterogeneous; the inner layers are copper oxide whereas the outer layers are alkaline salts of copper sulphate.

Their protective characteristics depend on their chemical composition, adhesion to the base metal, thickness, porosity, crystalline structure, etc (Rosales et al., 1999).

The in situ Pourbaix technique is a non-destructive method that allows evaluating the protectiveness of a patina through measurement of its electrochemical potential (Pourbaix, 1969, 1978, 1982, Van Muylder et al, 1976). With the object of analysing the evolution of the patina protectiveness by means of this technique the variation of the electrochemical potential with time was determined.

2. Methods

Measurements were made on different coloured zones of metallic sculptures belonging to the historical patrimony of La Recoleta Cemetery, which has been exposed to the atmosphere for almost a century:

- The El Karma sculpture (Figure 1) by Troiano Troiani was artificially patinated prior to exposition in 1927 (Cicileo et al 2004). On this statue measurements have been monitored at two years' intervals from 2000 to 2004, as a diagnostic method of the sculpture conservation state.
- The Mausoleum to Adolfo Alsina, by Margarita Bonnet, erected in 1915 (Figure 2). On this monument the sculptures La Ciencia and El Trabajo have been selected for measurements, in order to compare protectiveness of the different coloured areas and determine the best criterion and intervention procedures. Micro-cleaning tests were made removing particle deposits and incrustations. Detergent was used to eliminate surface dirt and xylol to degrease, whereas the black crusts were carefully picked with scalpels (Cicileo et al 2002). Monitoring of E_{sce} values have been performed at two years intervals from 2002 to 2004.
- El Cristo Central, by Zonza Briazo (1914) (Figure 3). Measurements of E_{sce} values have been started in 2004.

The selection criterion was based on the characteristic pathologies determined for each material in the sculpture set of the La Recoleta Cemetery (a Historic Protected Area of Buenos Aires City). The research work was initiated with El Karma and further the Mausoleum to Adolfo Alsina was added to compare two different aesthetic intentions previously described, on the same material. This year El Cristo was included to study the same material and aesthetic intention but in another microclimate. The different colour of the patinas formed on La Ciencia and El Trabajo for the same material depend from slight differences in microclimate parameters. These involve more or less sheltered surfaces with distinct access to the atmospheric pollutants, with the same orientation in respect to the cardinal points (resulting in almost the same temperature, time of wetness by rain, dew or water condensation, etc). However, the effect of the various inclinations, amount of open exposure on convex areas, the occlusion of pollutant from washing by rains in concave regions, all create a set of diverse conditions giving as a result different patina colours and electrochemical potentials that can be seen comparing Tables 2 and 3 (Vera et al. 2003).

The Pourbaix's technique of electrochemical potential measurement was extensively applied for patinas on steel development and protectiveness evaluation. We compared the protectiveness of various coloured patinas on bronze measuring their electrochemical potential evolution in time, providing a figure to help decide the best procedure for the conservation treatments. The main points are:

- the more stable and protective the patina is, the more stable is E_{sce} during the 90 s used for measurements;
- more stable/protecting patinas produce the higher values for E_{sce};
- a stable patina on copper base alloy could be defined when E_{sce} change no more than 30 mV in two yearly consecutive measurements (Cicileo et al 2004)

The portable arrangement used for in situ potential measurements consists of a glass tube fitted with a reference saturated calomel electrode (Esce = 242 mV/SHE) in one end. The other end, closed with a cotton piece soaked in distilled water, is applied to the zone whose potential is to be measured, through a saturated NaCl solution bridge. A voltameter connected the reference electrode to a small bare metal area, (locally cleaned from its corrosion layers in only one point), to establish the electrical contact for the many potential measurements throughout the whole structure.

After testing the measurement time needed to get stationary values we chose to perform them at 30, 60 and 90s. An initial value at t = 0 s gave values almost always decreasing with time, because not all the available diffusion ways through the patina have been flushed with water. This can be seen in the first row of Table 4, only included for comparison purposes. Further readings up to 90 seconds showed almost stable potential values for most patinas on Cu base alloys. Moreover, from 30 to 90s the direction of the change trend gave us valuable information about the patina behaviour as a good or bad protective barrier. According to our experience, not only with copper base alloys (of less than 100 μm thickness patinas) but also on weathering steels after three years outdoor exposure, the patinas of which were thicker than 200 μm, further measurements to 90s up to 1 h did not show a significant change with time because during the long rainy period all diffusion ways were flushed with water.

Protection corresponds to stable or increasing values associated with more noble potentials, while potential decreases or fluctuations indicate the passive film rupture allowing environmental attack on the metal. As an example of the two variations with time and the respective meaning, (see the last zone in Table 1), where the potential measured on the 'thigh' show a decrease during the measurement time, indicating that the patina is unstable, while its potential decrease from Year 2000 to 2004 demonstrates a passive effect decrease.

In a previous paper (Rosales et al, 1999), protectiveness was attributed rather to the morphology or barrier effect of the patina protecting the structure than to its chemical composition. For that reason no point to point comparison was performed between electrochemical potential measured and available X-ray information. Only few data could be compared in this non-destructive evaluation.

The chemical composition of different coloured areas of the sculptures was already determined in a previous work (Cicileo et al., 2004) by means of EDX and x-ray diffraction analyses. Black areas, yellowish green areas partially exposed to rainwater and light green areas directly exposed to rainwater were analysed.

Figure 1. El Karma

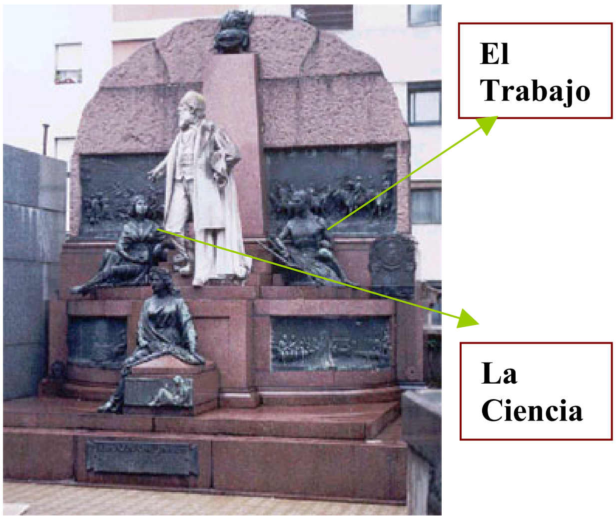

Figure 2. Alsina Monument

Fig 3. Cristo Central

3. Results and Discussion

The results of three series of *in situ* potential measurements with two years' intervals on different coloured areas of the El Karma sculpture are presented in Table 1. In the black zones higher potentials were observed, especially compared with those of the green zones completely exposed to the action of atmospheric agents, for example the area of the left thigh. After the two years' interval a general potential decrease was observed, especially in the exposed green areas. Differences amongst distinct areas of various stability potential were found in zones in contact with other metals, as on aluminium rivets and casting heterogeneities. On these latter areas it was meaningless to perform the mentioned measurements, because of the lack of a comparable patina formed on distinct metallic substrata, as verified on the left thigh area in Table 1.

Table 1. Three series of *in situ* potential measurements (E_{sce} (mV)) with 2 years' intervals on the El Karma sculpture.

Zone	**Colour**	**Year**	**E(mV) 30 s**	**E(mV) 60 s**	**E (mv) 90 s**
Ear interior	Black	2000	208	213	215
		2002	160	162	162
		2004	165	164	164
Forehead	Greyish green	2000	175	174	172
		2002	163	162	162
		2004	77	83	91
Chin	Green	2000	165	160	156
		2002	145	143	141
		2004	159	155	153
Left hand palm	Black crust	2000	153	150	147
		2002	165	164	163
		2004	182	179	179
Right hand (Al rivet)	White	2000	020	009	005
Left thigh	Yellowish green	2000	164	158	156
		2002	107	100	90
		2004	24	24	37

The Pourbaix technique was used as a diagnosis and monitoring test with time for El Karma sculpture whereas for La Ciencia and El Trabajo the objective was to determine the best criterion for intervention procedures. The highest potential decrease with time observed for La Ciencia as compared to El Trabajo (Tables 2 and 3), is a consequence of the least exposure to pollutant and atmospheric factors of El Trabajo, due to its more protected microclimate than La Ciencia. In the two latter sculptures micro-cleaning tests removed particle deposits and incrustations. In some zones a bluish green patina was found underneath the black crust after chemical cleaning and mechanical detachment. The characteristics of that patina corresponded, according to the historical testimony documents of the monument, to the original patina. Also the same potential measured confirms that green patinas of the same electrochemical behaviour are found in both cases. However, it is not always clear if a black surface product is a patina or a crust, unless there is the possibility of having enough material to undergo X-ray diffraction.

Table 2. Two series of *in situ* potential measurements (E_{sce} (mV)) on Alsina Monument, El Trabajo sculpture.

Zone	Colour	Year	E (mV) 30 s	E (mV) 60 s	E (mV) 90 s
Knee	Green (not cleaned)	2002	173	173	170
		2004	99	98	98
Abdomen	Black	2002	236	236	236
		2004	165	166	165
Abdomen	Green (after scalpel elimination of black crust)	2002	134	126	119
		2004	115	116	117
Right pectoral	Black	2002	214	215	215
		2004	130	127	126
Right pectoral	Bluish green (after scalpel elimination of black crust)	2002	154	154	153
		2004	116	114	113
Head	Black	2002	180	180	180
		2004	114	113	112
Head	Black (after scalpel elimination of black crust)	2002	142	140	139
		2004	91	92	91

Table 3. Two series of *in situ* potential measurements (E_{sce} (mV)) on Alsina Monument, La Ciencia sculpture, at 2 years' intervals.

Zone	Colour	Year	E (mV) 30 s	E (mV) 60 s	E (mV) 90 s
Forehead	Grey	2002	140	131	125
		2004	87	91	94
Right side of the book	Black	2002	222	224	227
		2004	236	241	250
Left shoulder	Black (not cleaned)	2002	203	202	202
		2004	168	170	180
Left shoulder	Green (after scalpel elimination)	2002	147	146	145
		2004	133	133	133
Feet	Green	2002	163	168	175
		2004	117	118	120
Arch of the foot	Olive green	2002	155	156	156
		2004	107	110	115

After mechanical removal the black crusts gave higher stable potentials within the 90s measurement than those in the underlying patina. In the left shoulder of "La Ciencia", for example, the underlying green patina gave stable potentials near 150 mV, whereas the potentials on the black crusts were around 200 mV, as shown in Table 3. After the two years' interval the high potentials of the black crusts remained, whereas the potentials of the green patinas decreased, mainly on the greyish green areas exposed to rain, like the zone of the forehead of “La Ciencia” allegory (Table 3).

In “El Cristo Central”, not all the black areas correspond to black crusts. They are limited to the areas sheltered from the rain. Measurements shown in Table 4 demonstrate that not only green but also black areas show a patina behaviour with similar electrochemical potentials.

Table 4. First series of *in situ* potential measurements (E_{sce} (mV)) on “El Cristo Central” sculpture, June 2004.

Zone	Colour	E (mV) 0 s	E (mV) 30 s	E (mV) 60 s	E (mV) 90 s
1Base front mantle	Black	156	153	152	151
3Right hand, running off	Green-greyish	112	120	122	120
7 Left hand, running off	Shiny black	134	122	125	128
10 Back, thin film, intense running off	Light green	80	70	56	58
12 Under green area, near basis (with wax)	Ochre area	129	125	123	120
14 Ear, running off	Green	102	100	99	98
15 Front	Shiny black	95	86	92	91
16 Left chest	Black area	129	127	128	127
17 Previous area after cleaning	Green area	122	120	120	119
22 Left shoulder, thin layer	Green-greyish	64	65	71	72

Measurements on areas of rain running off show low protectiveness, as in zones Nº 10 and 22. As opposed to what was observed in the three previous sculptures the measurements performed on black areas of El Cristo show a patina behaviour resulting from the similitude of their readings in respect to green areas. This is also similar to the author’s aesthetic intent. Green-black running off was artificially performed in the origin, as can be seen in zones Nº 1/12, Nº 3/7 and Nº 14/15. After cleaning the black areas the measurements show a potential decrease, as shown in zones Nº 16/17.

EDX and x-ray diffraction analyses showed that the black areas of the different monuments have similar composition. They revealed a high proportion of Si and Al, from particulate material, mainly composed of Al silicates. EDX analyses of particulate material have been reported (Bogo et al. 2003) showing the presence of Cl and Fe elements involved in black crusts. The green exposed areas also presented large Cl content because of the atmospheric pollutants incidence. X-ray diffraction analyses revealed that these areas were mainly composed of brochantite ($Cu_4(SO_4)(OH)_6$), atacamite ($Cu_2Cl(OH)_3$) being also present. Cuprite and other copper oxides presence was detected in the yellowish green areas.

4. Summary of the intervention proposals

In all the work the black areas should be analysed to separate the crust from black patinas, to allow treatment in different ways, according to their potentials. From Tables 1 to 4 the increased protectiveness of the crusts, characterised by almost stationary values during the 90s measurements and decrease after their elimination, can be observed. However, the underlying patina potential drops to the same value on different areas. This seems to be characteristic of the original patina formulated by the sculptor. It also evidences a similar protectiveness along the almost constant readings during measurements from 30 to 90s.

A clear difference appears between black areas in more protected zones with respect to more exposed zones to rain, sun, pollutants, etc. (higher and lower potentials respectively). Their cleaning results in an underlying patina with high to low protectiveness (more or less noble potential value), evidence of the negative effect of the atmospheric agents.

1. For the case of "El Karma" and "El Cristo Central" sectored treatments are proposed: black areas removal to recover the original underlying colour, as well as patina restoration on grey areas through use of the artist's original formulation. In this way the patina quality would be recovered in the differently affected areas (air quality, surface morphology and orientation, exposition angle with respect to atmospheric agents and pollutants, etc.) from past decades; differentiating sheltered from exposed regions. The intervention would recover the aesthetics of the work at the moment of its outdoor installation. The potential unit of the work would be established respecting the underlying patina below the black areas as witness of the passage of time.
2. For the metallic sculptures of the Mausoleum A. Alsina, also a sectored treatment is proposed according to the exposition type of areas. Thus, the suggestion involves black area elimination maintaining the underlying patina in sheltered areas, and patina restoration on most exposed regions. The patina would then maintain the sculptor's proposal and the transformations that have occurred since the creation of the piece up to our conscientious updating.

5. Conclusions

Each work requires a particular intervention according to the aesthetic perception designed by the sculptor.

Black crusts preserved historical dating of the surface treatments until the 1970s.

The *in situ* Pourbaix technique provides a useful tool for comparative evaluation of patina protectiveness from the environment and time impact. It also allowed us to design the best procedure for patina repair and its further protectiveness control.

The different coloured areas (green- black- grey) in the same work and their behaviour, including the post-cleaning time, determined a differentiated restoration and further protection for each case.

The intervention policies in La Recoleta cemetery for metallic sculptural heritage must consider the work as a *potential unit* from the artistic *aesthetic-temporal* proposals to the *physical reality* of the material and its environment.

References

Almeida, E., Ferreira, M. (1997) *Corrosão Amosférica- Mapas de Portugal*- INETI.

Arroyave, C., Morcillo M. (1995) *The effect of nitrogen oxides in atmospheric corrosion of metals*, Corros. Sci., 37, 2, pp 293-305.

Bogo, H., Otero, M., Castro, P., Ozafrán, M.J., Kreiner, A., Calvo, E.J., Martín Negri, R., (2003) *Study of atmospheric particulate matter in Buenos Aires city*, Atmospheric Environment, 37, pp 1135-1147.

Brandi, C., (1988) *Teoría de la restauración*, Alianza Forma. Madrid. Pág 29-34.

Cicileo, G., Rosales, B. and Crespo, M. (2002) *Análisis in situ de pátinas formadas sobre monumentos de bronce expuestos a la intemperie*, LATINCORR 2003, Santiago, Chile, October 20-24, pp 735-741.

Cicileo, G., Crespo, M. and Rosales, B. (2004) *Comparative study of patinas formed on statuary alloys by means of electrochemical and surface analysis techniques*, Corros. Sci., 46, 4, pp 929-953.

Crespo, M; Orsetti, A; Rosales, B; De Maio, B.; Ronco, A. (2000*) El deterioro del patrimonio escultórico* Rev. Gerencia Ambiental Año 7, Nº 66, 456 - 465. Buenos Aires. Argentina.

Crespo, M., (2002) *Lecturas de una transformación - Diagnóstico Histórico*"II Seminario Forum-UNESCO Universidad y Patrimonio. El Rol de La Universidad en La Formación, difusión y Conservación del Patrimonio. Buenos Aires Argentina. pp 10. In press
.
Crespo, M., (2001) *Deterioro del patrimonio escultórico y su relación con el receptor*. Encuentro Nacional de Investigación en Arte y Diseño. CD-ROM 3pp. La Plata. Argentina. pp 35
.
Fitzgerald, K. P., Nairn, J. and Atrens, A., (1998) *The chemistry of copper patination*. Corros. Sci., 40, 12, pp 2029-2050.

Graedel, T.E., Nassau, K., Franey, J. P., (1987) Corros. Sci., 27, 7, pp 639-657
.
Masamitsu, W., Yashiuro, H., Tohru, T., (2003) *Differences between corrosion products formed on copper exposed in Tokio in summer and winter*, Corros. Sci., 45, pp 1439-1453.

Oescht, S., Faller, M.,. (1997) *Environmental effects on materials: the effect of the air pollutants SO2, No2, NO and O3 on the corrosion of copper, zinc and aluminium*. A short literature survey and results of laboratory exposures, Corros. Sci., 39, pp 1505-1530.

Pourbaix, M. (1969) *Une Methode Electrochimique Rapide de Predetermination de la Corrosion Atmospherique*, Rapport Technique CEBELCOR 109, R. T. 160.

Pourbaix, M. (1969) Rapport Technique CEBELCOR N° 160.

Pourbaix, M. (1978) Proc.7th. International Congress on Metallic Corrosion, Rio de Janeiro, 3, 1181.

Pourbaix, M., Van Muylder, J., Porubaix, A. and Kissel, J. (1982) *Atmospheric Corrosion*, Hollywood, Fla., 1980. John Wiley & Sons, Inc., 167-177.

Rosales, B., Vera, R., Moriena, G., (1999) *Evaluation of the protective properties of natural and artificial patinas on copper*. Part I. Patinas formed by immersion, Corros. Sci., 41, pp 625-651.

Strandberg, H., (1998) *Reactions of copper patina compounds*- I Influence of some air pollutants. II. Influence of sodium chloride in the presence of some air pollutants. Atmospheric. Environment., 32, 20, pp 3511-3526.

Tribute Commision to the Memory of Dr. A Alsina. Archivos Mausoleo al Dr A. Alsina de Monumento Biblioteca del Senado de la Nación. 1915.

Van Muylder, J. and Pourbaix, M. (1976) Rapport technique CEBELCOR, N° 72.

Vera, R., Rosales, B.M. and Tapia, C.(2003) *Effect of the exposition angle in the corrosion rate of plain carbon steel in a marine atmosphere*. Corr. Sci. 45, 321-337.