

Electrochemical Characterization of Patinas Formed on a Historic Bell from the Cathedral Museum of Campeche-México, World Heritage Site

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The Cathedral of Nuestra Señora de la Inmaculada Concepción, from the historical City of San Francisco de Campeche (México), is considered one of the most important Novo Hispanic Baroque buildings constructed between 1650 and 1760 by the Spanish colonizers in the South East of the country. Actually the Cathedral is part of about 1500 constructions included into the UNESCO's Cultural Heritage awarded by the City in 1999. Its Diocesan Museum of Sacred Art has a significant collection of invaluable historic artifacts from colonial period, such a bronze bell dating from 1650. This study was carried out in order to evaluate the electrochemical behavior of natural patinas formed over the bell surface by using Electrochemical Impedance Spectroscopy (EIS). In situ test under simulated acid rain media and complementary surface analysis such SEM/EDS, XRD and metallography allowed an assessment of the behavior of this ancient bronze bell under atmospheric incidences along the time. The results suggest the closer interaction between metallic alloy composition, environmental conditions and the protective abilities of its patinas.

Keywords: bronze alloys, patinas, EIS, materials characterization, historic bell.

1. INTRODUCTION

The bells have been used in Europe at least from the V century, but it is known that Egyptian and oldest Asiatic cultures, Romans and Greeks also used these artifacts. By the time of the early

middle age, were established the first bell manufacturing technologies based on empirical knowledge related to metallurgy, then art decoration was also highly developed and a better understanding of the acoustic properties of bell for religious ceremony. By the XVI century the total art of bell-casting was well established all over Europe [1]. In America, Spanish colonizers impose the use of bells as a part of liturgical ceremonies and were installed in towers of churches and Christians temples.

In addition, in some cities such as San Francisco de Campeche in México, the bells were commonly used as alert signal in defensive systems, for example in doors, walls, watch towers and residences of the military complex that protected the city again pirate attacks between the XVII and XVIII centuries. Cast iron, brass and bronze were metallic alloys typically used to elaborate this kind of artifacts. Bronze was the favorite alloy for manufacture of foundry sculptures and others decorative artifacts because this metal reproduces each mold details and can show high corrosion resistance [2, 3].

Atmospheric corrosion affects metallic cultural heritage exposed to both outdoor and indoor environments which can change their appearance and stability in the course of time [4]. In low polluted environment or controlled indoor conditions, the metallic aspect of bronze alloy is usually maintained or gradually changed with time to a brown black shade because of the formation of corrosion layers also called patinas. However, the gradual evolution of corrosion products exhibits different colors. The initially formed copper oxide are responsible for gradually more brown-black surface appearance, whereas different basic copper sulphates and chlorides make the surface greenish [5, 6].

The natural evolution of patinas and its protective capability depends on chemical composition and adherence properties, crystalline structure, evolution of the surrounding atmosphere (including climatic factors), pollutants and indirect biological activity [7, 8]. The long time required for formation of patinas on unprotected bronze on the atmosphere is variable. It takes approximately 20–100 years in rural areas, up to 10 years in urban areas, and several years in marine environments [3].

Conservationists consider a real importance the study of patina in spite of, it is a register of the historic material interaction with the environment. Also, the patinas represent an esthetic value but can also deteriorate in a polluted environment [4]. In this order, there are a general interest in patinas conservation because they are considered protector films under stable conditions, nevertheless, any modification on its properties or in the surrounding environments could to generates several damages to artifact integrity [3, 6-8].

The present study is focused in the electrochemical behavior of natural patinas formed on the historic bell Purísima Concepción Menor, that actually is exposed at the Diocesan Museum of the Cathedral of Nuestra Señora de la Inmaculada Concepción (at San Francisco de Campeche, México). The bell, dated from 1650 shows a well-developed patina formed along the time, first during its long exposure to the natural marine atmosphere of the City, secondly, at the actually indoor conditions of the museum.

2. EXPERIMENTAL

2.1. Materials Preparation - The Bell

The bronze bell “Inmaculada Concepción Menor” dated form the year of 1650 corresponding to the Baroque period. It has symmetric axial geometry, with 60 cm height, 50 cm i.d. and about 50 Kg

weight. The bell presents two cordons surrounding the crown and two more at the bead line. In the body of the bell can be observed geometric ornamental motives forming a cross, and on the opposite side, the figure of the *Inmaculada Concepcion* (Figure 1). In 2005, it was deposited at The Sacred Art and Diocesan Museum of the Cathedral of San Francisco de Campeche City, where actually is exhibited.



Figure 1. The bronze bell Inmaculada Concepción Menor, at The Sacred Art and Diocesan Museum of the Cathedral of San Francisco de Campeche City

2.2. Electrolytic Media

The electrolytic solution used during the experiment was an artificial acid rain solution, prepared considering a mixture of anionic and cationic salts (ultrapure grade), according to next concentration: NaCl (2.48 ppm), KCl (0.48 ppm), $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (2.98 ppm), MgSO_4 (0.60 ppm), NH_4NO_3 (0.88 ppm), Na_2SO_4 (1.90). Solution was acidified with some drops of H_2SO_4 (38 % v/v), until a final pH of 4.9. This formulation was previously defined from wet/dry deposition studies carried out at San Francisco de Campeche City [9].

2.3. Scanning Electron Microscopy coupled to Dispersive X Ray Emission (SEM/EDS)

A small fragment of 0.25 cm^2 was retired from the bell. A portion was included in transversal position into epoxy resin. Prior to the measurements, the sample was mechanically grounded and polished until 2500 grade of abrasive paper. Next, the sample was observed, without previous treatment in a coupled SEM/EDS Philips XL30 system operated at 20 KeV, work distance of 10 mm and incidence angle of 0° . A coupled SUTW-Saphire system with a resolution on 131 eV, was employed in order to detect the characteristics X ray emitted by the sample.

2.4. Metallographic analysis

Small samples were prepared using silicon carbide paper (220-1500 grit size). Finally, were polished with diamond paste (35 μm). Etching solution was prepared with additions of the following chemicals: 5% of ferric chloride in ethylic alcohol (98 ml) and hydrochloric acid (2 ml) during 30 seconds. Microstructural observations were carried out with Inverted Metallograph Inspection Microscope (OLYMPUS PMG-3).

2.5. X Ray Diffraction (XRD)

Corrosion products were retired by scrapping from dark greenish and reddish-brown patinas located at internal and external areas of the bell (Figure 3). Crystalline phases were identified in a Brag-Brentano D5000 X ray Diffractometer (Siemens D5000), and analyzed under the following conditions: Cu K α radiation ($\lambda=1.5416$ Å) and operational conditions of 25 mA and 35 kV at a step size of $2^\circ/2\theta/\text{min}$ in the $2-60^\circ$ range 2θ .

2.6. Electrochemical Impedance Spectroscopy (EIS)

For electrochemical measurements, ACM Field Machine potentiostat was employed. The reference electrode was a saturated calomel electrode (SCE), while the counter electrode was a platinum wire. EIS study was carried out “*in situ*”, by adapting a conventional three-electrode microcell for a register area of 1 cm^2 (Figure 2). Experiments were performed using one milliliter of artificial acid rain solution in contact with a saltbridge. Impedance measurements were carried out at E_{corr} at room temperature, with a signal amplitude perturbation of 10 mV and frequency range of 30 kHz to 5 mHz. For analyzing the experimental data, curve fitting method was used.

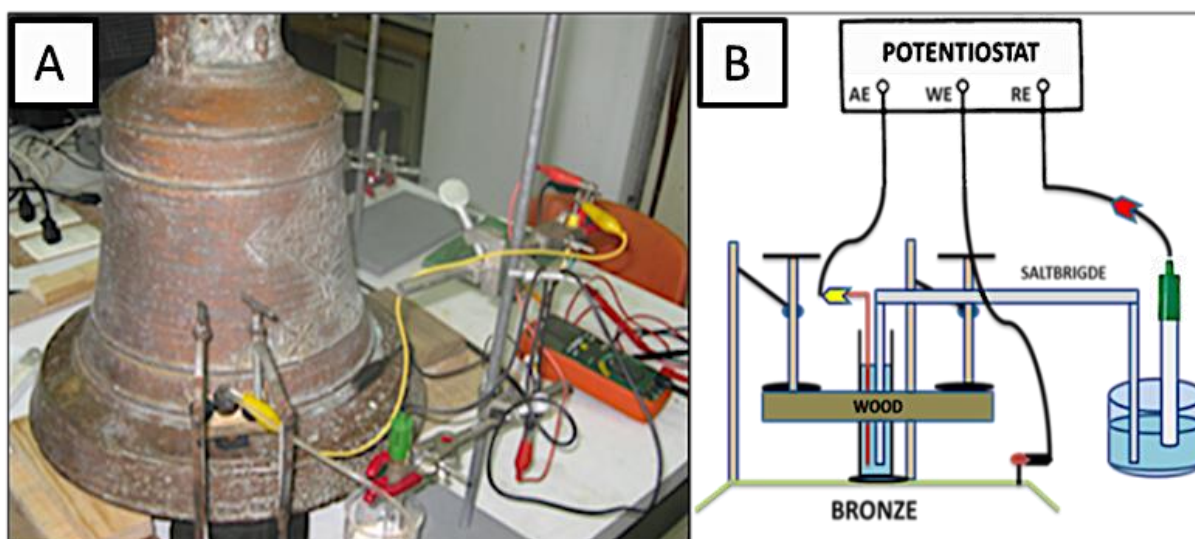


Figure 2. (A) Experimental arrangement, (B) Esquematic representation of measurement design

3. RESULTS AND DISCUSSION

3.1. Visual observation

Visual examination of the body of the bell showed evidence of atmospheric corrosion on the metallic alloy. Uniform reddish-brown patina cover external areas of the artifact, while the presence of compact dark greenish film is mainly localized in the crown and ornamental motives, such as relieves and bead line cordons, where appear some cracks. Under the sound ring, superficial dissolution of metal is noticeable (Figure 3). Also some white earthy deposits can be observed in several sections of the bell, which is probable consequence of environmental exposure [2, 10]. On internal area, relatively protected from direct environmental factors, patina acquires predominant dark greenish aspect. These surface structures are usually called noble patina due to their very protective properties, its aesthetic and pleasant aspect [11]. Color of patinas refers a particular formation of environmental condition. Studies carried out in closer areas of the Cathedral of San Francisco de Campeche City categorized the atmospheric aggressively such as medium category for Cu, Zn, and Fe, and medium to high for Al according to ISO International Standard (time of wetness of 3721 hours per year, SO_2 1.47 $\text{mg}/\text{m}^2\cdot\text{d}$ and Cl 18.08 $\text{mg}/\text{m}^2\cdot\text{d}$) [12, 13]. Under these conditions the high relative humidity is the key factor on atmospheric corrosion, in spite of the low levels of corrosive pollutants supplied to the atmosphere.

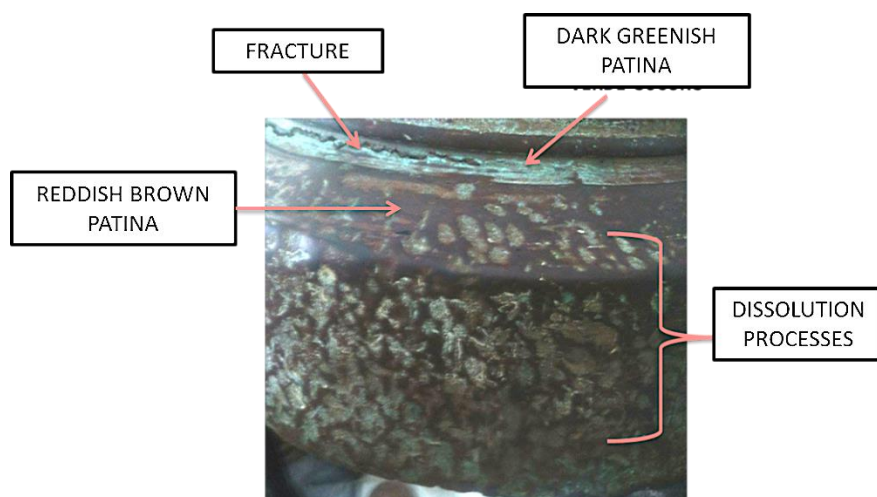


Figure 3. Visible surface alterations on the bell

3.2. Compositional and structural characterization

EDS elemental determination on the bulk material of the artifact reveals a binary bronze alloy composed by a wt% proportion of 6.26 Sn and 93.74 of Cu. Not historical data about thermal treatment or manufacturing process of the alloy are available, but these proportions coincide with those observed in some ancient bronze artifacts manufactured according traditional procedures established during the Middle Age at Europeans workshops [3, 14-16].

Figure 4a shows an image of the revealed bulk alloy surface. Its typical reddish color contrast with black structures corresponding to the presence of pores due to the probable lost of impurities

during the etching procedure or the occurrence of defects during the casting of the piece. Also, the presence of packing cuprous oxides microcracks, is a clear signal of intergranular corrosion. Distributed around the α - solid solutions some grey islands about 0.3 mm are clearly perceptible.

An increasing in magnification (Figure 4b) allowed the observations of α -phase Cu typical of casting alloys. Dark areas observable in the microstructure corresponds to $\alpha+\delta$ eutectoid phase formed during solidification, favoring the presence of this rich tin interdendritic precipitates. According Cu-Sn phase diagram, this eutectoid phase appears during cooling step of casting as a consequence of microstructure segregation in low tin bronzes (between 5-15 % Sn) [17-18]. Several authors indicate that to $\alpha+\delta$ eutectoid phase is common in historic bronzes [1, 19, 21-22]. On the other hand, Omid et al., and Scott., refer to grey islands as a probably Cu/Sn intermetallic precipitated also formed during cooling step of casting, with higher content of tin. [18, 20].

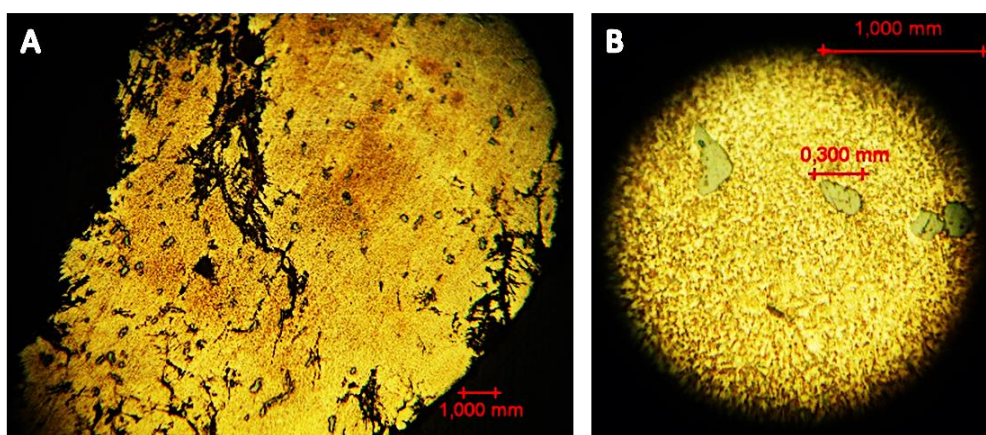


Figure 4. Microstructure of the bronze alloy. a) 10x, b) 50x

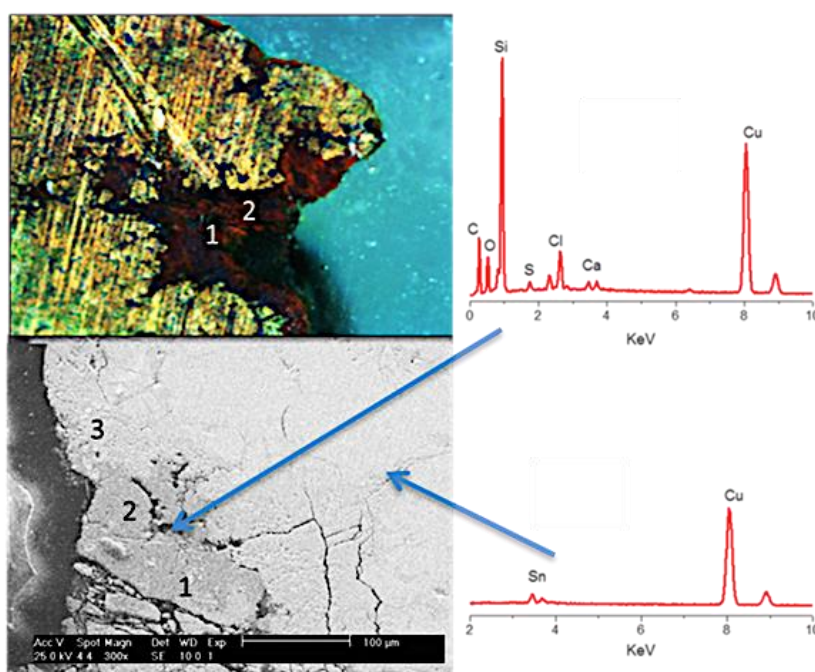


Figure 5. Transversal section of corrosion layers. up) dark greenish, down) reddish brown.

Figure 5-up, shows an optical micrography (5x) corresponding to a transversal section of the corroded fragment retired from the bell. Corrosion layer has compact aspect, but there can be differentiating two areas corresponding dark greenish and reddish brown layers (1 and 2, respectively). The observation of the transversal sections by SEM microscopy (300x), reveals a corrosion layer about 115 μm thickness covering the bulk material (Figure 5-down). Porous structure of the patinas is noticeable.

Patinas show a two type of stratified structure: the first one, seems to be the called Type I [4, 23- 24]. According to Robiolla *et al.*, it is formed by an external greenish layer of atacamite followed by second reddish-brown layer of cuprite over the bulk material [11]. The second one, is called Type II. The same authors indicate that it is formed by the superposition of atacamite over an internal layer of cuprite followed by a final dark greenish layer of nantoquite, over the sensitized bulk material (Figure 5b). In both cases, all corrosion products present a fragile porous structure, that in the case of the SEM image seems be low adherent. The image also demonstrates that microcracks are connected to the layer/alloy interface. Because of that, ionic species can diffuse to originate intergranular or transgranular corrosion on cracks, stressing the alloy structure as have been observed previously on ancient bronzes [14, 25].

Table 1 shows elemental composition of corrosion products presents on both the surface and the transversal section of the patinas. Due to bronze alloys suffers preferential dissolutions of copper into natural atmospheres; exogenous elements can be entrapped into corrosion layers. Most of them, incorporated to corrosion products, keep an important role on its stability under atmospheric condition.

Table 1. EDS Elemental composition (wt%) of surface and transversal section of corrosion layers.

Element	Surface of patina				Transversal section			
Measure Point	1	2	3	4	1	2	3	4
C	34.20	39.75	38.16	19.69	34.68	9.55	8.34	42.85
O	18.80	37.80	31.82	36.40	8.56	18.88	9.92	15.55
Na	-	1.96	1.64	-	-	-	-	-
Mg	1.23	1.21	0.96	0.25	-	-	-	-
Al	1.23	1.21	0.96	0.25	-	-	-	-
Si	2.31	10.5	2.01	-	0.85	-	-	0.45
S	1.96	0.71	0.43	-	1.06	-	-	-
Cl	0.70	0.77	1.56	0.78	2.96	13.16	1.21	1.69
K	0.66	0.55	0.42	-	-	-	-	0.22
Ca	15.59	4.57	10.12	38.9	1.89	0.71	11.99	5.52
Fe	1.05	0.42	0.72	-	-	-	-	-
Cu	23.5	1.69	11.5	3.73	50	57.7	68.53	33.71

*- Under detection limit

Figure 6-up, shows a SEM image (300x) captured from the transversal section of representative samples retired from the bell fragment. The bulk microstructure of the material shows small irregular empty spaces probably formed by nonmetallic impurities eliminated during sample preparation. Other

imperfections also observed were a series of longitudinal microcracks forming during casting due to dendritic segregation. During corrosion, the bulk material suffers modifications because of the expansion of corrosion layers from surfaces and the diffusion of corrosive species into localized areas of the alloy such as cracks, where oxides such as cuprite, nantokite and tenorite, in dependence of environmental conditions could precipitate (Figure 6-down) [14, 20, 25-27].

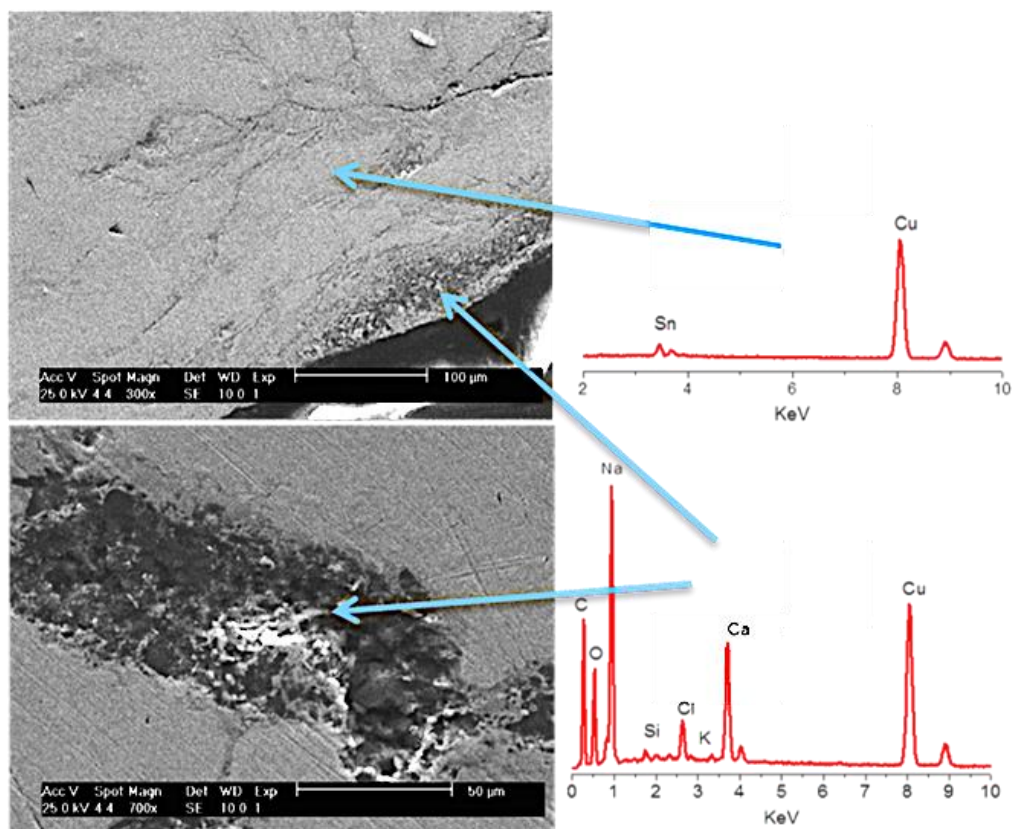


Figure 6. Metal base (up) and deposits (down)

Basic components of bronze patinas such as Cu, O and Cl were observed (Table 1). Surface Dark green patinas are characterized by high content of chloride. On the other hand, the particular combination of calcareous soils, urban environment and the proximity to the coastline allow atmospheric transport and deposition of particles over the bell. C, Na, Mg, Al, K, Si and Ca are soil elements content in dust particles, while S and Cl are tracer of atmospheric pollutant, the first one is consequence of fossil fuel combustion, while, the last one, is a natural component of marine aerosols. Their presence is indicative of certain corrosive capabilities of the atmosphere affecting metallic infrastructure. Secondary source of C can be attributed to biomass [14, 23-25]. In transversal sections, elements such as C, O, Ca, and in higher proportions Cl and Cu are predominant. Here, the higher content of Cl and the extended time of witness lead higher copper dissolution rates. Because of that these element is launched from the bulk materials forming copper chlorides [3, 11, 28]. Not Sn was observed on any corrosion layer.

3.3. Identification of crystalline phases

Crystalline phases identified by DRX in corrosion products are presented in Table 2. Predominant phases from copper dissolution were cuprite (Cu_2O), atacamite ($\text{Cu}_2\text{Cl}(\text{OH})_3$) and nantokite (CuCl). The presence of calcite (CaCO_3), sanidine (KAlSiO_8), quartz (SiO_2) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) in corrosion layers is probable consequence of bell contamination. They are mineral components of soil particles or construction residues incorporated to patinas [7, 15]. The calcium oxalates, Whewellite ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$) and Weddellite ($\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$), are a group of biominerals associated to metabolic residues of organisms formed by reaction of oxalic acids with calcium carbonate under humid conditions. These compounds have been observed in mortar samples from several historic building of San Francisco de Campeche City, including the Cathedral [9]. It can be assumed that residues of such materials are the probable source of calcium oxalates because of deposition processes.

Table 2. Crystalline phase identified in patinas of the bell

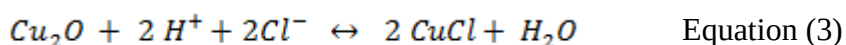
Crystalline phase	Redish Brown	Dark greenish
Atacamite ($\text{Cu}_2\text{Cl}(\text{OH})_3$)	+	+
Calcite (CaCO_3)	+	+
Cuprite (Cu_2O)	+	+
Gypsum($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)	+	+
Nantokite (CuCl)	+	-
Sanidine (KAlSiO_8)	+	+
Quartz (SiO_2)	+	+
Weddellite ($\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$)	+	+
Whewellite ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$)	+	+

*+ observed, - not observed

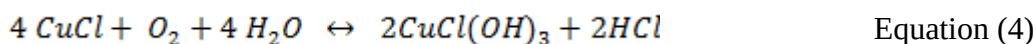
Reddish brown cuprite is the first adherent corrosion product formed on bronze alloys due to surface oxidation on not polluted environmental conditions according the next reaction [11, 14, 25, 29-30].



The cuprous chloride nantokite observed on external layers have been considered a non-passive film [11, 14]. Chloride accumulation corresponds to an autocatalytic process similar to the called “bronze disease” [11, 28]. On rich chloride environments, nantokite manifestations is preceded by the anionic mechanisms of cuprite formation, then it promotes the copper dissolution controlled by two probable mass transfer mechanisms: diffusion of metallic ions toward dissolution (Equation 2), or in the other way, chloride ions diffusion toward interface (Equation 3) [11, 14, 31-34].



Nevertheless, because of its high hygroscopicity, nantokite results unstable under water and oxygen activity, then reacts to form atacamite, the dark green oxide observed on the bell. It proceeds according to the next reaction [27-28, 35-37]:



Atacamite tends to increase its volume, leading the apparition of powder alteration, increasing the porosity in corrosion layers, forming microcracks and allowing the loss of material [11, 29-30]. Several authors propose two mechanisms of patinas formation during bronze disease: first a traversal structure of dark green patinas adhered to the surface of the bell represented in Figure 8 (Type 1). It consists in the first cuprite layer strongly adhered to metal surface followed by a second stable layer of atacamite, protectress again environmental agents. [11, 28].

On the other hand, on external areas of the bell, the characteristic red brown patina are structured by a primary layer of nantokite, the stable chloride corrosion product adhered to bulk metal. Nantokite formation is allowed by anionic diffusion mechanisms of chloride ions always presents in the marine atmosphere of the City [12]. Next the cuprite oxide film followed by an atacamite layer, in contact with the environment [3, 11, 14, 27].

3.4. Electrochemical Impedance Spectroscopy characterization

Figures 7a-d, shown the Nyquist diagrams and their corresponding simulation obtained from the *in situ* electrochemical measurements carried out over both the dark greenish and the reddish to brown areas of the external and internal surface of the bell. On the other hand, Table 3 shows electrochemical parameters obtained from equivalent electrical circuit during EIS simulation.

EIS data from dark greenish and reddish brown areas shows characteristic depressed capacitive semicircles on high frequencies, centered on the real axis, which trends to form second semicircles on intermediate frequencies followed by a straight path on lower frequencies. This behavior may be due to the probable presence of electrochemical process controlled by mechanisms of charge transfer and diffusion of ionic species across the protective corrosion layers adhered to the metallic surface, and the presence of atmospheric deposits [39-40]. On this experiments, EIS semicircle diameter can be considered proportional to charge transfer resistance (R_{ct}) of the bronze alloy in presence of patinas (Figure 8). Higher resistances were observed in presence of Type I patinas with values between 90000 and 43000 $\Omega \text{ cm}^2$, while the lowers were between 1270 and 37000 $\Omega \text{ m}^2$ under the Type II (Table 4). Is noticeable that ingress of chloride ions arrives until bulk alloy surface, provoking a catalytic effect, responsible to modify interfacial structure and generation of nantokite ompound.

On the other hand, the resistance of cuprite layer (R_c) were of 31500 and 72200 $\Omega \text{ cm}^2$, (Table 3). Cuprite is the characteristic compact reddish brown patina of homogenous structure presents on bell surface. The opposite behavior was observed for the less protective patina (Type II), conformed by cuprite and nantokite with low resistance values (R_{c+n}) of 6125 $\Omega \text{ cm}^2$ y 451 $\Omega \text{ cm}^2$. It is consequence of a more porous structure, because of that; patinas do not protection availabilities [11, 28].

According previous studies, the urban-marine atmosphere of San Francisco de Campeche City leads extended time of wetness and deposition of marine aerosols directly from the coastal line [12]. Under these conditions, the protective availability of corrosion layers diminish, and therefore increase on deterioration rate of the bronze alloy can be observed as occurs in other coastal zones [42-44]

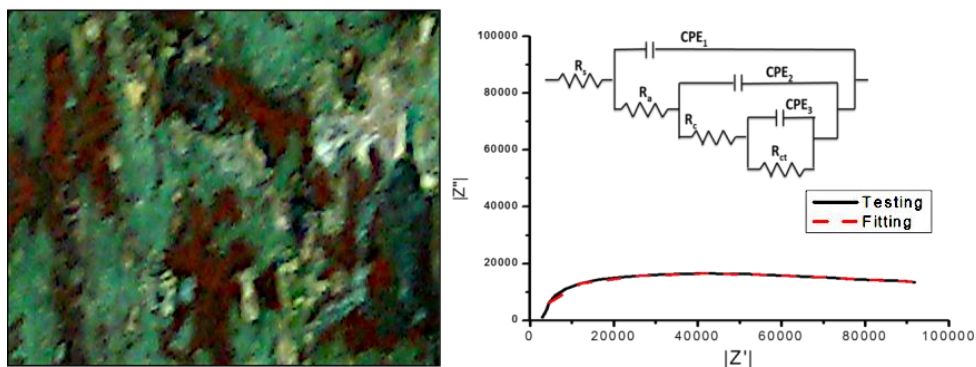


Figure 7a. Nyquist and fitting diagram and equivalent circuit for ‘in situ’ impedance obtained from dark greenish patina at the external surface of the bell (Type I)

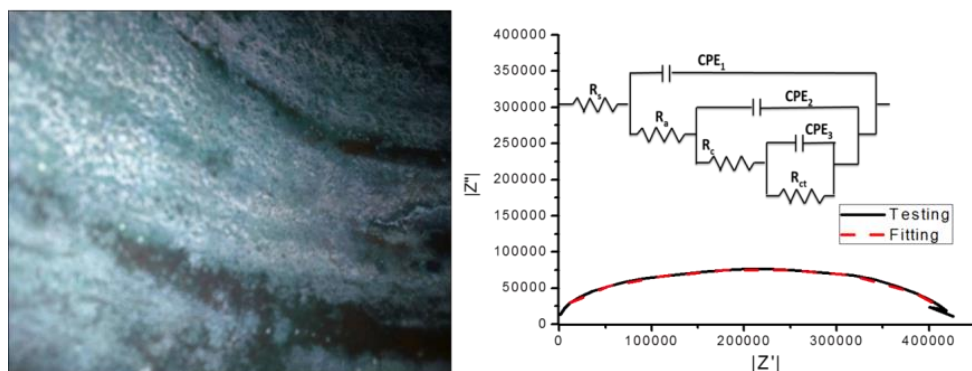


Figure 7b. Nyquist and fitting diagram and equivalent circuit for ‘in situ’ impedance obtained from dark greenish of the internal surface of the bell patina (Type I)

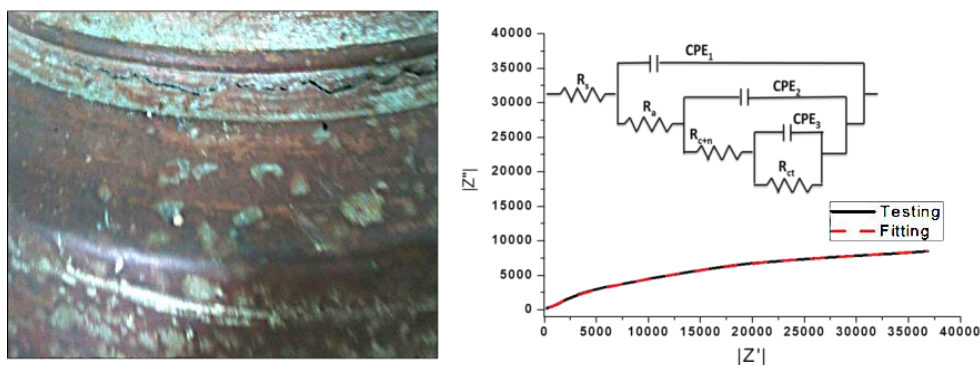


Figure 7c. Nyquist and fitting diagram and equivalent circuit for ‘in situ’ impedance obtained from a brown patina (Type II)

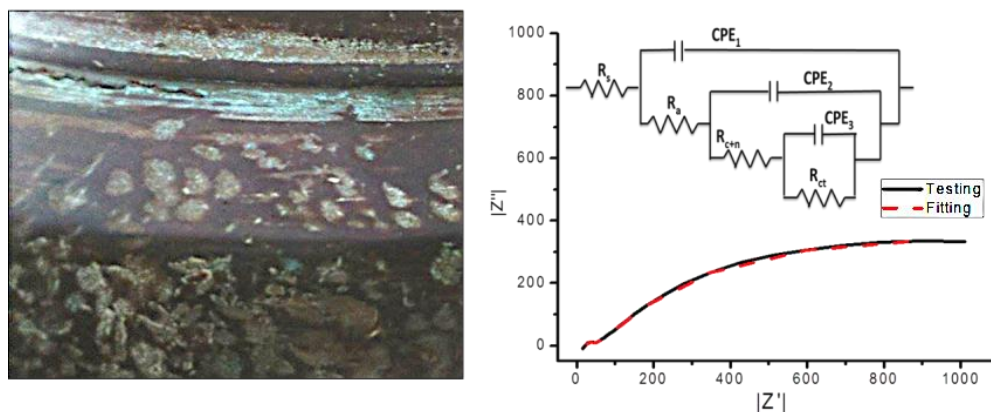


Figure 7d. Nyquist and fitting diagram and equivalent circuit for ‘in situ’ impedance obtained from a reddish brown patina (Type II).

Table 3. Electrochemical parameters obtained from equivalent electrical circuit during EIS simulation

R_s (Ω/cm^2)	C_{at} (F/cm^2)	CPE_1 (n)	R_{at} (Ω/cm^2)	C_{cup} (F/cm^2)	CPE_2 (n)	R_c (Ω/cm^2)	C_{dl} (F/cm^2)	CPE_3 (n)	R_{ct} (Ω/cm^2)
In dark greenish patina at the external surface of the bell (Type I)									
31.27	3.6×10^{-9}	0.98	2.05×10^4	2.0×10^{-6}	0.54	3.1×10^4	5.4×10^{-7}	0.65	9.0×10^4
In dark greenish at the internal surface of the bell patina (Type I)									
9.52	5.7×10^{-10}	0.98	8.256×10^4	2.3×10^{-8}	0.63	7.2×10^4	2.6×10^{-7}	0.81	4.3×10^5
R_s (Ω/cm^2)	C_{at} (F/cm^2)	CPE_1 (n)	R_{at} (Ω/cm^2)	C_{cup} (F/cm^2)	CPE_2 (n)	R_{c+n} (Ω/cm^2)	C_{dl} (F/cm^2)	CPE_3 (n)	R_{ct} (Ω/cm^2)
In brown patina at the external surface of the bell (Type II)									
89.48	1.9×10^{-8}	0.98	372.4	5.4×10^{-5}	0.59	6125	1.31×10^{-5}	0.40	3.7×10^4
In reddish brown patina at the external surface of the bell (Type II)									
24.59	3.3×10^{-6}	0.97	22.83	2.4×10^{-3}	0.55	451	2.51×10^{-4}	0.58	1270

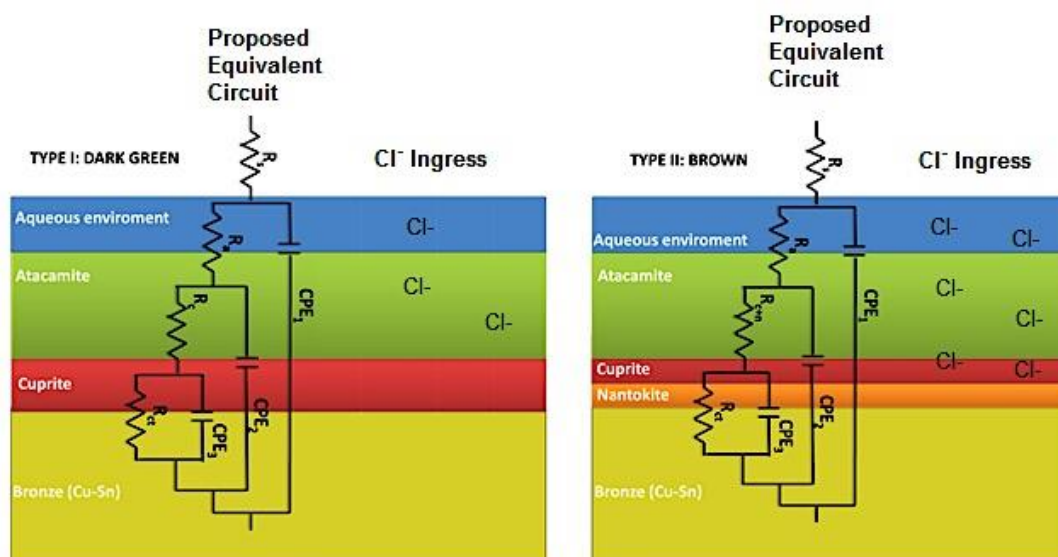


Figure 8. Proposed equivalent circuit for the characteristic impedance spectra associated to both Type one and Type II patinas.

The figure 8, shown the proposed equivalent circuit where R_s is associated to solutions resistance, R_a represent the opposition to the current flow of the atacamite external layer, CPE_1 is the constant phase element related to its capacitance and constant phase elements and capacitance arrangements R_c-CPE_2 , γ and $R_{c+n}-CPE_2$ can be associated to the type I and II patinas, while the double layer charge transfer resistance and phase elements are R_{ct} and CPE_3 , respectively [15, 38-39]

4. CONCLUSIONS

Elemental and microscopical analysis allowed the identification of Cu/Sn alloy conformed by a dendritic microstructure characteristic of ancient casts. Other chemical elements identified in bronze patinas indicate the complex interaction of metallic artifacts with the environment along the time.

Crystalline phases identified on alloy patinas were cuprite (Cu_2O), atacamite ($Cu_2Cl(OH)_3$) and nantoquite ($CuCl$). They are characteristic of copper dissolution of bronze in marine atmospheres. External deposits such as calcite ($CaCO_3$), sanidine ($KAlSiO_8$), quartz (SiO_2), gypsum ($CaSO_4 \cdot 2H_2O$), weddellita ($CaC_2O_4 \cdot H_2O$) and whewellita ($CaC_2O_4 \cdot 2H_2O$) were also observed.

Charge transfer resistance results directly proportional to the protective availability of patinas. In this study, the higher resistance (between $10000 \Omega \text{ cm}^2$ to $400000 \Omega \text{ cm}^2$), corresponded to the dark greenish Type I patina, while lower resistances (between $40,000 \Omega \text{ cm}^2$ y $1.500 \Omega \text{ cm}^2$) were observed on such areas covered by the reddish to brown Type II patina.

Chloride ion diffusion results determinants on cuprite stability over alloy surface. It is important to note that the presence of nantokite reduce protective ability of patinas across the interface with metallic surface.

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