



Influence of the environment on the atmospheric corrosion of bronze

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Received 8 January 2004; accepted in revised form 30 April 2004

Key words: bronze, marine atmosphere, patina composition, patina morphology, pollutant levels, urban atmosphere, weight losses

Abstract

This paper presents a comparative study of the atmospheric corrosion of bronze samples exposed for 12 months, at two sites: an urban atmosphere with intense traffic, in the city of Lisbon, and a rural marine atmosphere, Cabo da Roca, with a high degree of humidity, strong winds and high levels of chlorides all the year round. Exposures were started in the summer. Levels of SO₂, NO₂ and chlorides, in both atmospheres, were measured during the period of exposure. Climatic data for both sites was also collected and analysed. Weight losses and weight gains of samples with 4, 6, 8 and 12 months of exposure were measured and the average corrosion rates calculated. Chemical composition and morphology of the patinas formed during the exposure period, at both sites, were compared as well as the morphology of the corroded surfaces. Significant differences, related to the level of pollutants and meteorological variables, were found.

1. Introduction

It is well known that copper and its alloys form thin layers of corrosion products when exposed to the atmosphere, generally brownish-green or green-bluish. These layers are designated as 'patinas', a name derived from the green patina crust often found on Roman dishes or patens. Copper patinas are generally regarded as aesthetically pleasing and much of the use of bronze and other copper alloys in architecture and sculpture is based on their patina properties. Once the patina is established it tends to be extremely stable and to become a permanent part of the building or object to which it is attached.

Several studies have demonstrated that among other climatic factors, humidity plays a major role, especially in the presence of aggressive species. Deliquescent corrosion products or salts, which attract water vapour, become soluble above a critical humidity depending on the types of corrosion products [1–6]. On the other hand, atmospheric pollutants are transported principally in two ways, by dry and wet deposition processes, therefore, humidity, precipitation and wind are important parameters defining the nature of the electrolyte at the metallic interface.

The morphology of the patinas, their adhesion and degree of porosity are dependent on the climatological conditions, nature and level of pollutants. The chemistry of patina formation is important in this context [7, 8]. In

a recent paper, Watanabe et al. [9] report differences in the corrosion products formed on copper during a one month exposure time in summer and in winter.

The purpose of this study is to attempt to relate the formation of bronze patinas to the characteristics of the atmosphere in which they are formed. The deposition rates of SO₂ and of chlorides and the levels of NO₂ were monitored continuously, at the two sites, during the period from August 1999 until July 2000. Meteorological data during that period, for both sites, was also collected and analysed. Weight gains and losses of samples exposed to both atmospheres were measured and the average corrosion rates calculated. The morphology of the surfaces of bronze samples with twelve months of exposure was analysed.

2. Experimental details

The two test sites were the terrace of the C1 building of the Faculty of Sciences of University of Lisbon, at Campo Grande, 38° 45' N (longitude), 9° 9' W (latitude) and 100 m altitude. The other site was Cabo da Roca, a promontory on the West Coast of Portugal, located at 38° 47' N; 9° 30' W, at an altitude of 140 m above sea level.

The period of exposure was from August 1999 (summer time) until July 2000. Bronze samples were cut from bronze with the composition given in Table 1. Samples of 7.5 cm × 3.5 cm were prepared for exposure

Table 1. Nominal composition of the bronze samples (%)

% Cu	% Sn	% Zn	% Pb	% P	% Ni	% Fe	% Al	% Mn	% Sb
88.02	11.25	0.21	10.19	0.195	0.083	0.02	10 ⁻⁴	10 ⁻⁴	5 × 10 ⁻³

(triplicates for weight loss measurements and singles for surface analysis). The specimens were first polished with emery paper (grit no. 1 and no. 0), then washed several times with distilled water and finally dried and degreased with acetone. Samples for weight loss determinations were weighed before and after exposures. After exposure, corrosion products were removed following the procedure described by the ISO/DIS 9226 [10], then washed several times with distilled water, degreased and dried with acetone, before being reweighed. An analytical, Mettler AE 260 Delta range balance was used. Coupons were exposed in panels mounted according to ISO/DIS 8565 [11], with an angle of 45°.

Air samples for the analysis of SO₂, NO₂ and chlorides were collected continuously, at both sites, during the exposure period. SO₂ was determined as sulphate by the PbO₂ adsorption method, as described by Amber [12] following ISO/DIS 9225 [13]. Chlorides were collected via the humid candle methodology as described in ISO/DIS 9225 [13, 14]. The NO₂ was collected with passive samplers as described by Shooter [15].

The X-ray spectra of the corrosion products were obtained with a Philips 1710 diffractometer equipped with a graphite monochromator coupled to a vertical goniometer PW 1820. The X-ray source was operated at 40 keV and 30 mA. SEM/EDS studies were performed with a scanning electron microscope Jeol mod. 7 MS-35 C coupled to an X-ray diffractometer Noran Voyager operating at 20 keV.

3. Results and discussion

3.1. Levels of pollutants and climatological data of the test sites

Table 2 gives the monthly average deposition rates of SO₂ and of chlorides and the levels of NO₂ at both sites, during the period of this study. The deposition rates of SO₂, were in the same range at both sites, between 14 and 46 mg m⁻² day⁻¹ in Lisbon (Campo Grande), and

between 9 and 46 mg m⁻² day⁻¹ at Cabo da Roca. Levels of SO₂ are in agreement with those reported by Fontinha and Salta [16] for the period from 1985 to 1993, and by Almeida and Balmayor [17] for the period 1989–1992. In Lisbon, during the period from August 1999 until July 2000 the highest values of SO₂ were observed in December, January, February and March, (winter time), while at Cabo da Roca, the highest values were recorded in February, May, June and July. At Cabo da Roca during those months winds blew mostly from the SE and NE (continental winds).

To find possible correlations between the composition and morphology of the bronze patinas and the climatic conditions, meteorological data for both sites were collected and analysed (Table 3). At Campo Grande (C.G.), during the summer, the less aggressive climatic conditions and the reduction in the number of vehicles entering the city (summer holidays) certainly both contribute to lowering the levels of SO₂ recorded during this season. Winds blew mostly from the SW during September 99 and April 2000 and from the NW during August 99, February, March and May 2000. The data in Table 3 also shows that the times of wetness, TOW, are fairly high at Cabo da Roca, particularly during August, September and October (summer). At Campo Grande the highest values of TOW were registered in December 1999, January and April 2000. The highest levels of SO₂ were recorded during those months.

The deposition rates of chlorides, at Campo Grande, were in general quite low as would be expected, ranging between 6 and 15 mg m⁻² day⁻¹, while at Cabo da Roca, they were quite high, between 58 and 278 mg m⁻² day⁻¹. The annual average values were 122 and 9 mg m⁻² day⁻¹, at Cabo da Roca and Campo Grande, respectively, leading to the classification of these atmospheres as S₂ and S₁ according to ISO/DIS 9223 [18]. The highest level of chlorides, at Campo Grande (15 mg m⁻² day⁻¹), was recorded in April 2000, exactly the month in which the wind blew mostly from the seaside (640 times from SW).

Concerning the levels of NO₂, in the urban atmosphere values between 31 and 93 μg m⁻³ were recorded with the

Table 2. Levels of SO₂, NO₂ and chlorides, in Lisbon (C.G.) and at Cabo da Roca (C.R.) from August 1999 until July 2000

		Aug. 99	Sep. 99	Oct. 99	Nov. 99	Dec. 00	Jan. 00	Feb. 00	Mar. 00	Apr. 00	May 00	Jun. 00	Jul. 00
SO ₂	C.G.	17	23	26	20	30	46	28	33	14	21	24	28
(mg m ⁻² d ⁻¹)	C.R.	–	16	14	9	11	24	46	27	18	39	29	45
Cl ⁻	C.G.	9	13	7	6	6	6	6	7	15	9	12	13
(mg m ⁻² d ⁻¹)	C.R.	–	106	72	58	95	61	278	68	84	217	95	209
NO ₂	C.G.	–	31	53	68	71	93	61	59	38	36	32	29
(μg m ⁻³)	C.R.	–	6	6	5	7	11	7	3	3	6	6	5

C.G. Campo Grande; C.R. Cabo da Roca.

Table 3. Climatological data for the atmosphere of Lisbon, Campo Grande (C.G.) and Cabo da Roca (C.R.) from August 1999 until July 2000

	Average temp. /°C		Precipitation/ days month ⁻¹		TOW /h month ⁻¹		No. of hours with wind blowing from							
							SW		NW		SE		NE	
	C.G.	C.R.	C.G.	C.R.	C.G.	C.R.	C.G.	C.R.	C.G.	C.R.	C.G.	C.R.	C.G.	C.R.
Aug. 99	22	18	4	8	312	750	239	43	618	112	4	706	24	705
Sep. 99	20	17	11	9	258	684	295	96	438	124	22	534	52	533
Oct. 99	17	16	16	10	432	714	464	150	150	145	16	176	204	176
Nov. 99	13	12	5	4	210	324	0	4	198	131	4	389	479	389
Dec. 99	11	11	15	6	480	576	294	139	170	283	0	254	314	254
Jan. 00	10	11	9	5	348	468	42	26	134	148	40	208	448	208
Feb. 00	13	12	0	0	252	552	8	2	480	108	10	803	150	804
Mar. 00	15	13	10	3	174	174	131	39	320	354	185	231	252	232
Apr. 00	14	12	27	12	432	432	640	140	150	430	114	2	114	2
May 00	18	–	6	0	–	–	60	34	558	117	52	772	52	772
Jun. 00	21	–	2	1	–	–	228	18	512	208	90	266	90	266
Jul. 00	23	–	3	2	–	–	148	36	635	161	167	823	157	823

C.G. Campo Grande; C.R. Cabo da Roca; TOW: no. of hours with an HR ≥ 80% and $t \geq 0$ °C.

highest value ($93 \mu\text{g m}^{-3}$) recorded in January 2000. On the other hand, in the marine atmosphere, the levels of NO₂ were quite low all the time, but again the highest value ($11 \mu\text{g m}^{-3}$) was registered in January 2000. It is worthwhile to mention that during that month winds blew most of the time from the NE (Table 3).

The analysis of the levels of pollutants and the climatological data led to the following classifications for the two atmospheres: P₁, S₁ and τ_4 , for Campo Grande; P₁, S₂ and τ_5 for Cabo da Roca (ISO/DIS 9223 [18]). The average temperature was not much different at both sites, ranging between 10 and 23 °C.

3.2. Corrosion rates

Figure 1 gives the weight losses and weight gains of bronze samples as a function of exposure time at both test sites. Identical periods of exposure led to much higher weight losses at Cabo da Roca. The weight losses follow almost linear relationships described by Δm (g m^{-2}) = $38t^{0.4}$ and Δm (g m^{-2}) = $14t^{0.2}$ (t expressed in years), for the bronze samples exposed at Cabo da Roca and Campo Grande, respectively. The lower value of the exponent indicates more protective properties of the film formed.

The measurements of weight gain allow the amount of insoluble corrosion products present on the samples after exposure to be inferred. During the period under evaluation, values in the range 1.3–2.4 and 7.2–13.6 g m^{-2} for samples exposed at Campo Grande and Cabo da Roca, respectively, were measured. The percentage of adherent products was calculated using the weight gains and weight losses, that is, $[(\Delta m(+)) \times 100 / (\Delta m(-))]$. The percentage of adherent products at Campo Grande varies from 11 to 11.5%, remaining at a constant value during the period from the 8th to 12th month of exposure while, at Cabo da Roca, the percentage increases over the exposure period, from

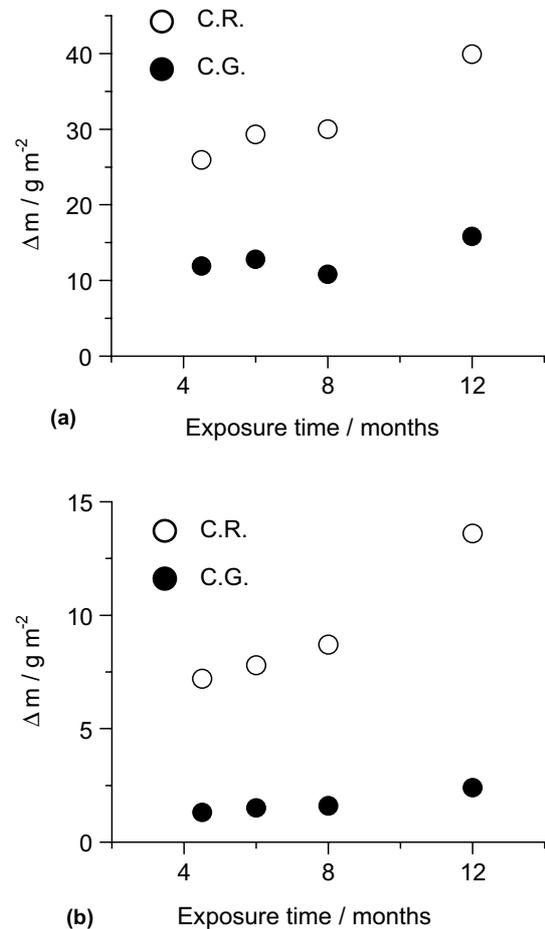


Fig. 1. Plots of (a) weight losses and (b) weight gains as a function of exposure time: (●) Campo Grande; (○) Cabo da Roca.

28 to 35%. This indicates continuous formation of corrosion products that remain on the surface of the exposed samples.

Figure 2 gives the evolution of the average corrosion rates of bronze samples at both sites. V_{CORR} starts with

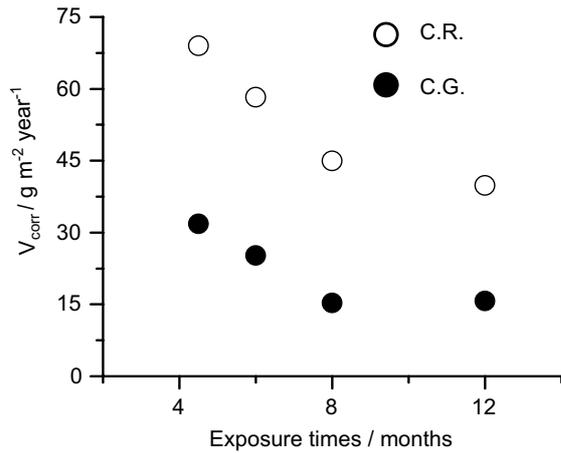


Fig. 2. V_{corr} along the exposure period at Campo Grande (●) and Cabo da Roca (○).

quite high values and then slows as time advances reaching values of 40 and 16 $g\ m^{-2}\ year^{-1}$ after 12 months exposure, at Cabo da Roca and Campo Grande, respectively. This behaviour is typical of situations leading to the formation of passive films. Under identical conditions, copper samples have presented higher corrosion rates than bronze samples [19–21].

The corrosion rates of copper samples during a one-year period lead to the classification of the two sites in the categories C₄ and C₅ for Campo Grande and Cabo da Roca, respectively (ISO/DIS 9223 [18]).

3.3. Patinas on bronze samples

3.3.1. Optical images

Optical images show:

- (i) Significant differences in the colour of bronze patinas: patinas formed on bronze samples exposed in the urban atmosphere are much more brownish-green, while those formed on samples exposed in the maritime atmosphere are more green-bluish.

- (ii) Great differences on the morphology of the patinas: compact and uniform films on samples exposed in the urban atmosphere and nonuniform, loose and less adherent films with corrosion products scaling out on the surface on samples exposed in the marine atmosphere.

- (iii) Zones showing local corrosion on the bronze samples exposed in the marine atmosphere are well seen.

3.3.2. SEM images

The morphology of the corrosion products of bronze samples with 12 months exposure was observed by scanning electron microscopy (SEM). Global and local analysis of the corrosion products was performed by energy dispersive spectrometry (EDS).

Figure 3 shows an SEM image of a bronze sample exposed for 12 months in the urban atmosphere. Various regular structures are seen, such as, cubic structures but also irregular structures with various sizes. The EDS spectra identify S, O, Cl and Ca apart from Cu and, in lesser amounts, Si, Al, Mg and Na.

The spectra of the samples exposed at Cabo da Roca (Fig.4(c)) present a high percentage of Cl (chlorides and/or hydroxy-chlorides). The other elements identified are Cu, O and elements such as Si and S (minor amounts) as well as Al, K, Ca, Mg and Fe. Figure 4(a) and (b) shows images of local structures on the patinas from bronze samples exposed at Cabo da Roca. According to the information given by the EDS spectra the structure in Figure 4(a) is most probably the structure of a chloride or hydroxy-chloride not well crystallized.

Table 4 gives data from EDS analysis of the corrosion products on bronze samples from both sites. The main differences in the elemental composition of the patinas formed in the two atmospheres are evident. Patinas from the maritime atmosphere show much higher percentages of chlorides while those from the urban atmosphere show higher percentages of oxides and sulfates. Elements such as Si, Al, Ca, K, Mg and Fe are

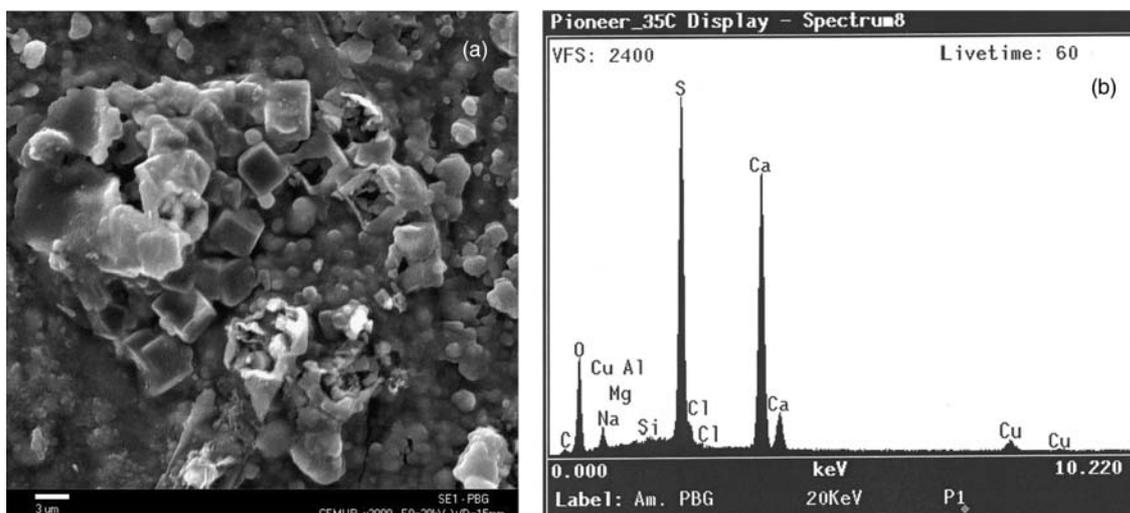


Fig. 3. (a) SEM micrographs of bronze samples with 12 months of exposure at the urban atmosphere and (b) the corresponding EDS spectra.

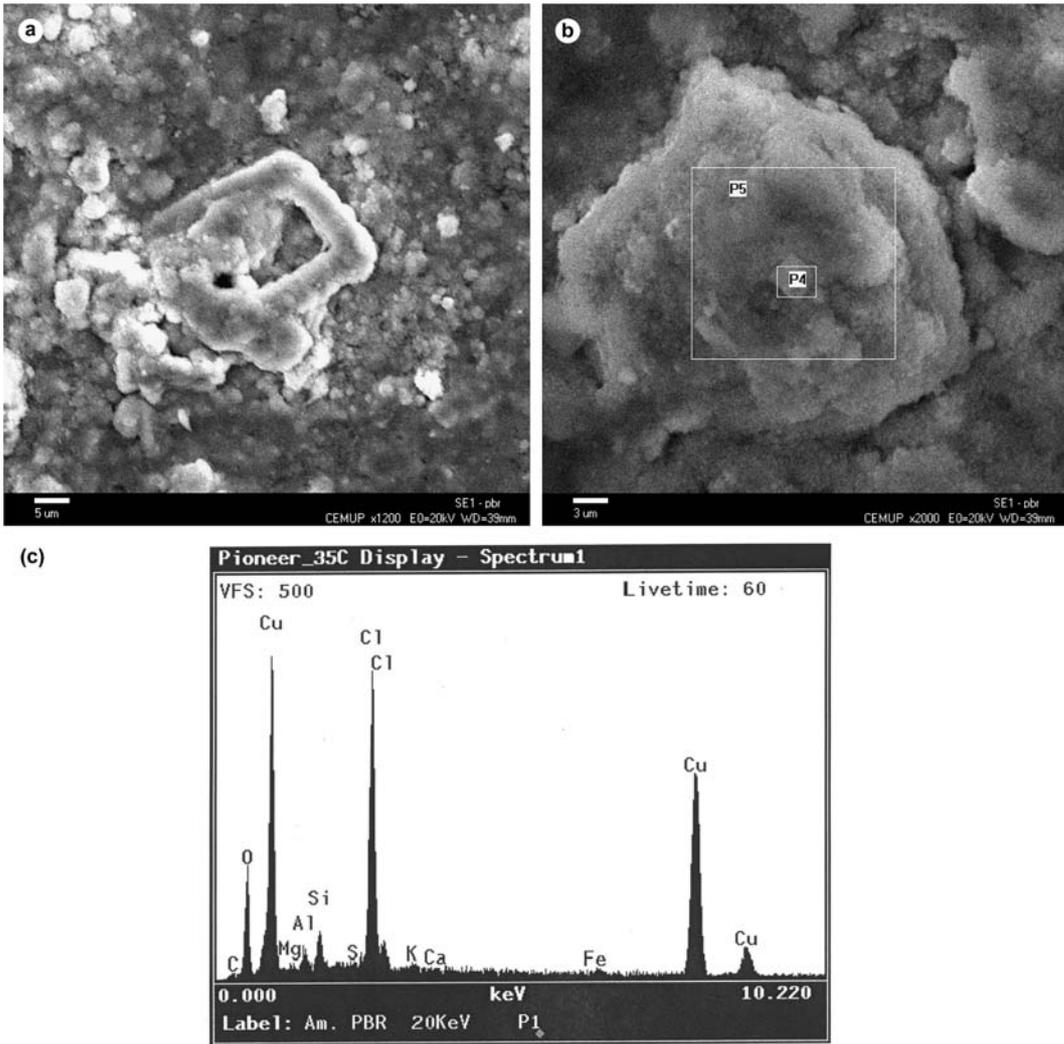


Fig. 4. (a) and (b) SEM micrographs of bronze samples with 12 months exposure at the marine atmosphere; (c) the EDS spectra of zone P5.

Table 4. Composition of the bronze patinas given by EDS

Elements /%	Cu	Sn	O	Cl	S	C	Si	Al	Ca	K	Mg	Fe
C.G	46.9	6.1	15.2	11.6	5.0	1.0	4.6	2.5	4.3	1.5	0.8	0.5
C.R.	35.1	–	12.6	39.7	1.5	1.3	4.4	2.1	0.8	0.8	0.9	0.7

present in a minor, but similar, percentage with the exception of Ca which has a higher percentage on the samples from the urban atmosphere. Sn has been identified only on samples exposed to the urban atmosphere (C.G.), and not on the samples exposed at Cabo da Roca. The percentage of O and Cu is higher in the patinas on samples exposed at Campo Grande, indicating, a higher percentage of copper oxides.

3.3.3. Chemical composition

X-ray diffraction allows the identification of the crystalline corrosion products. Figures 5 and 6 give the

evolution of the X-ray diffraction pattern of the corrosion products on samples with the indicated exposure times, from samples in the urban and marine atmospheres, respectively.

From the analysis of both sets of spectra it is possible to conclude that cuprite is the major product on samples from both sites. Samples from the urban atmosphere present high percentages of basic sulfates (brochantite and posnjakite) but also atacamite and paratacamite. On samples from the marine atmosphere, apart from cuprite, basic chlorides were found. Samples with twelve months exposure also show crystals of sodium chloride, silica and gypsum.

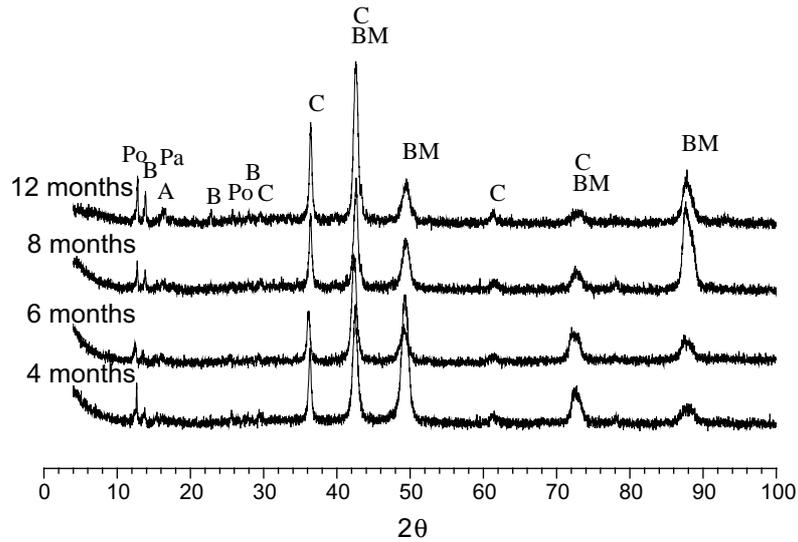


Fig. 5. X-ray diffractograms of the corrosion products on bronze samples with 4, 6, 8 and 12 months of exposure at Campo Grande. Key: (BM) base material; (Pa) paratacamite; (A) atacamite; (C) cuprite; (Po) posnjakite; (B) brochantite.

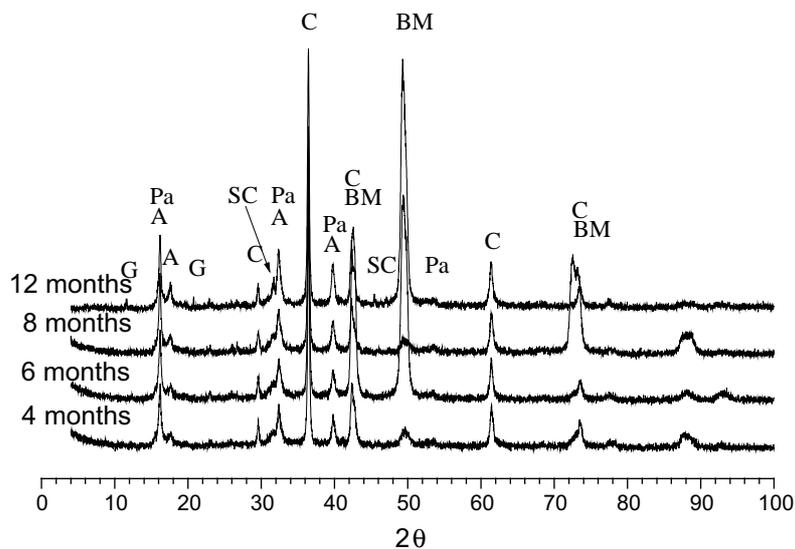


Fig. 6. X-ray diffractograms of the corrosion products on bronze samples with 4, 6, 8 and 12 months of exposure at Cabo da Roca. Key: (BM) base material; (Pa) paratacamite; (A) atacamite; (C) cuprite; (SC) sodium chloride; (G) gypsum.

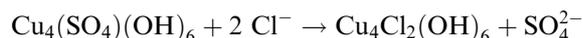
Table 5. Crystalline compounds on the patinas and their relative amounts on bronze samples with 6 and 12 months of exposure at Campo Grande (C.G.) and Cabo da Roca (C.R.)

Crystalline Compounds on the patinas	Exposure time 6 months		12 months	
	(C.G.)	(C.R.)	(C.G.)	(C.R.)
Cuprite, Cu ₂ O (red–brownish)	***	**	***	***
Brochantite, Cu ₄ SO ₄ (OH) ₆ (green)	**	–	**	–
Ponjakite, Cu ₄ SO ₄ (OH) ₆ ·H ₂ O (green)	**	–	**	–
Atacamite, Cu ₂ Cl(OH) ₃ (green)	*	**	**	**
Paratacamite, Cu ₂ Cl(OH) ₃ (green)	*	**	**	**
Sodium chloride, NaCl (white)	–	–	–	*
Silica, SiO ₂ (incolor)	–	*	–	*
Gypsum, CaSO ₄ (white)	–	–	–	*

*traces; **low percentages; ***high percentages.

Table 5 gives the relative amounts of the various corrosion products on samples from both sites.

Although EDS spectra identified S on bronze samples exposed in the marine atmosphere, the crystalline basic sulphates were identified only on samples exposed in the urban atmosphere. The absence of crystalline sulphates on bronze samples from Cabo da Roca may be attributed to the synergetic effects of chlorides and SO₂ in the presence of high quantities of chlorides. Brochantite may react with chloride leading to hydroxy-chlorides, that is:



4. Conclusions

As expected the levels of NO₂ were higher in the urban atmosphere with an annual average value of 50 against 6 μg m⁻³ in the maritime atmosphere. On the other hand, the deposition rate of chlorides was higher in the marine atmosphere with an annual average value of 110 against 9 mg m⁻² day⁻¹). At both sites a maximum value for the deposition rate of SO₂ (46 mg m⁻² day⁻¹), was recorded, in January at Campo Grande and in February at Cabo da Roca. The highest values seem to be related to the higher degrees of humidity and precipitation and also with winds blowing from the continent (NE and SE). The corrosion rates start at quite high values, then decrease almost linearly at a rate of about 1.25 and 3.7 g m⁻² month⁻¹ during the first eight months of exposure. After 12 months exposure average corrosion rates of 16 and 40 g m⁻² year⁻¹, from samples exposed in the urban and marine atmospheres, respectively, were recorded.

Patinas on bronze samples exposed in the urban atmosphere (Campo Grande) are more adherent than those of the corresponding samples exposed in the marine atmosphere. However, in the marine atmosphere the degree of adhesion increases with time and is higher than that observed with copper samples [19–21].

The main crystalline corrosion products on bronze samples exposed for one year in the urban atmosphere are cuprite, brochantite, posnjakite, atacamite and paratacamite, while those from the marine atmosphere are cuprite, atacamite and paratacamite.

Patinas on bronze samples exposed in the urban atmosphere are quite uniform, while those from the marine atmosphere are nonuniform; presenting scaling which may allow localized corrosion. In fact, after removal of the corrosion products, pits were observed on SEM images of the scaled areas.

Soluble nitrates may be present in the patinas [22, 23]. However, with the techniques used in this study they could not be identified. The absence of crystalline tin oxides is probably due to the formation of amorphous stannic oxide. Other inorganic salts such as nitrates and

carbonates, as well as organic salts, may be present in the patinas. Studies by infrared spectroscopy (FTIR) and ionic chromatography (IC) may be useful in the identification of such compounds.

Studies of the seasonal influence on the corrosion rates and corrosion products of bronze samples, particularly during short exposures started in winter and summer time, are in progress.

Acknowledgements

The financial support of the Portuguese Science and Technology Foundation (FCT) to Centro de Electroquímica e Cinética da Universidade de Lisboa, under the Operational Programme of Science, Technology and Innovation (POCTI), is acknowledged. The authors would also like to thank Dr Carlos Sá from CEMUP for the SEM/EDS facilities. Thanks are also due to Con-tibronzes S.A, for providing the bronze samples.

References

1. T.E. Graedel, K. Nassau and J.P. Franey, *Corros. Sci.* **27** (1997) 639.
2. P. Eriksson, L.-G. Johansson and J. Gullman, *Corros. Sci.* **34** (1993) 1083.
3. S. Feliu, M. Morcillo and S. Feliu Jr., *Corros. Sci.* **34** (1993) 415.
4. S. Oesch and M. Fuller, *Corros. Sci.* **39** (1997) 1505.
5. B.I. Rickett and J.H. Payer, *J. Electrochem. Soc.* **142** (1995) 3713.
6. M. Morcillo, B. Chico, L. Mariaca and E. Otero, *Corros. Sci.* **42** (2000) 91.
7. T.E. Graedel, *Corros. Sci.* **27** (1997) 7416.
8. K.P. Fitzgerald, J. Nairn and A. Atrens, *Corros. Sci.* **40** (1998) 2029.
9. M. Watanabe, Y. Higashi, T. Tanaka, *Corros. Sci.* **45** (2003) 1439.
10. ISO/DIS 9226 'Corrosion of Metals and Alloys. Method of Determination of Corrosion Rate of Standard Specimens for the Evaluation of Corrosivity' (ISO, Geneva, Switzerland, 1987).
11. ISO/DIS 8565 'Metals and Alloys. Atmospheric Corrosion. General Requirements for Field Tests' (ISO, Geneva, Switzerland, 1990).
12. R. Amber, British Standards Institute, Pt 4 B5 (1969) 1747.
13. ISO/DIS 9225, 'Corrosion of Metals and Alloys. Aggressivity of Atmospheres. Methods of Measurements of Pollution Data' (ISO, Geneva, Switzerland, 1987).
14. F.J. Rossotti and H. Rossotti, *J. Chem. Educ.* **42** (1965) 375.
15. D. Shooter, *J. Chem. Educ.* **5** (1993) A133.
16. R. Fontinha and M. Salta, *Ciência e Tecnologia dos Materiais* **13** (2001) 4.
17. E. Almeida and M. Balmayor, *Corros. Prot. Mater.* **18** (1999) 6.
18. ISO /DIS 9223 'Corrosion of Metals and Alloys. Classification of Corrosivity. Categories of Atmospheres' (ISO, Geneva, Switzerland, 1989).
19. A.C. Ramos, MSc. thesis, University of Lisbon, Portugal (2001).
20. I.T.E. Fonseca, R. Picciochi, M.H. Mendonça and A.C. Ramos, *Corros. Sci.* **46** (2003) 547.
21. R. Picciochi, A.C. Ramos and I.T.E. Fonseca, *Portugaliae Electrochim. Acta* **20** (2002) 77.
22. Y. Aoyama, *Werkst. Korros.* **12** (1961) 148.
23. D.W. Rice, R.J. Cappell and W. Kinsolving, *J. Electrochem. Soc.* **127** (1980) 891.