

ATMOSPHERIC CORROSION OF COPPER AND ITS ALLOYS

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Resumo: O cobre e as suas ligas, graças à sua boa resistência à corrosão atmosférica, têm sido largamente utilizadas na construção de elementos arquitectónicos decorativos, em componentes de edifícios (revestimento de telhados) e ainda em estátuas e artefactos diversos de monumentos. No entanto, o aumento da poluição atmosférica ocorrido nas últimas décadas levou a que os danos causados pela corrosão atmosférica nestes metais tenham vindo a ser mais significativos. Nesta comunicação são apresentados resultados obtidos num estudo de corrosão atmosférica que envolveu a exposição natural de cobre em diferentes atmosferas durante dez anos, incluindo a determinação das velocidades de corrosão, análise do tipo de produtos de corrosão formados, das alterações da superfície e da influência das condições atmosféricas (características climáticas e de poluição) nos mecanismos de corrosão. Faz-se ainda uma comparação da composição dos produtos de corrosão formados no cobre neste estudo de exposição natural com a composição das patinas formadas em estátuas de bronze e de latão de monumentos com várias décadas de exposição em atmosferas urbanas e urbana-marítima.

Abstract: Due to its good atmospheric corrosion resistance, copper and its alloys have been widely employed in a large number of building components like roofs, decorative elements and also in metallic sculptures and monuments, since centuries. However, the growth in atmospheric pollution over the last decades led to an increase of the damages caused by corrosion on these metals. In this paper, results obtained from a ten-year exposure in several atmospheres are presented, comprising corrosion rates, types of corrosion products formed, surface changes and the influence of the atmospheric conditions (climatic and pollution characteristics) on the corrosion mechanisms. The composition of the corrosion products formed is compared with that found in bronze and brass statues exposed to urban and urban-marine atmospheres for several decades.

Keywords: Atmospheric corrosion tests, copper, bronze, patina, corrosion products, kinetics

Introduction

Copper and its alloys are often chosen for usage in permanent external architectural applications due to its good atmospheric corrosion resistance. This behaviour results from the formation of a protective corrosion layer (*patina*), often considered of aesthetic value, which reduces the corrosion velocity through out the years. However, the presence of high contents of gaseous pollutants SO_x in the atmosphere and the presence of chloride ions aerosols, can change the protective nature of the pre-existing *patinas* or lead to the formation of less protective ones, increasing the expected corrosion velocity of copper.

With the purpose of studying the long-term corrosion behaviour of copper, an atmospheric corrosion study in different aggressive environments was initiated in 1985. The results obtained from this study during 10 years of exposure are presented in this paper. The study comprised corrosion rates and weight loss determinations, analysis of the corrosion products formed, surface changes and the influence of the atmospheric conditions (climatic and pollution characteristics) on the corrosion mechanisms.

Under the international project EUREKA EUROCORE-COPAL in the last three years different statues of copper alloys (bronze and brass) have been inspected for corrosion diagnosis. These monuments are between 30 and 200 years old.

The statues are located in urban environments with heavy traffic, one of them is also exposed to high marine influence. This study involved an extensive chemical analysis programme on samples collected from the different monuments.

The chemical composition of corrosion products of the bronze and brass statues is compared with the one obtained for the copper test specimens.

Material

Copper sheet of current fabrication was chosen for this study[1]. Table 1 shows its composition.

Table 1 – Alloy chemical composition by qualitative spectrographic analysis[1]

Elements concentration / %					
<i>Cu</i>	<i>Si</i>	<i>P</i>	<i>Al</i>	<i>Fe</i>	<i>Pb</i>
>99.5%	<0.1%	<0.1%	traces	traces	traces

The test specimens were cut from the metallic sheets of different materials into plates with size of 120mm x 200mm, having thickness of 0.85 mm.

Prior to exposure, all the specimens were degreased with an organic solvent and weighed to the nearest 0.01 g.

Exposure conditions

For this study, four sites in Portugal were chosen, representing urban, marine and industrial-marine atmospheres:

Roca, marine atmosphere, a promontory in the West Coast, 50 km far from Lisbon. Altitude 140 m, 10 m from the ocean. Frequently under dense fogs during all seasons of the year.

Barreiro, industrial-marine atmosphere, inside the industrial park on the roof of a one story building, surrounded by chemical plants (sulfuric acid, fertilizers, a siderurgy, etc.), close to a fuel burning power generation factory, near Lisbon, on the south banks of river Tagus. This site has undergone a substantial corrosivity change during the study, since the SO₂ content in the air has decreased, due to the closing of several factories (see Table 3).

Lisbon, urban atmosphere, on LNEC's roof, near the airport and roads of intensive traffic.

Alfanzina, marine atmosphere, a promontory in the South Coast (Algarve). Altitude 37 m, 10 m from the ocean.

During the first 7-8 years of exposure, *in situ* regular analysis of chloride and sulphur dioxide contents in the air were done by the wet candle and the lead dioxide methods, respectively. The results obtained are presented in Table 2. The climatic characteristics for the different localisation of the test sites were taken from data reported by the Meteorological Institute for the test site areas, during the period from

1985 to 1988. Table 3 shows the meteorological data. The time of wetness (TOW) presented was estimated from the temperature and relative humidity (RH) values, considering the number of hours with RH higher than 80% and temperature above 0°C.

The test specimens were mounted to porcelain insulators on racks of painted galvanised steel positioned at 45° to the horizontal, facing south, except at Roca where they are facing west to enhance the exposure to the saline spray. The lower row of test specimens is 0.75 m above ground.

Table 2 – Average Chloride and Sulphur dioxide deposition rates measured in the test sites during the period from 1985 to 1993

Site	SO ₂ / mg.m ⁻² .d ⁻¹	Chloride / mg.m ⁻² .d ⁻¹
Roca	6	194
Barreiro	136 ^a	38
Lisbon	14	7
Alfanzina	8	201

^a During the first four years of study (1985-1989) the average values reached 200 mg.m⁻².d⁻¹, but in the following three years (1990-1993) this value decreased to an average of 50 mg.m⁻².d⁻¹

Table 3 – Yearly average values for meteorological characteristics for test sites areas during the period from 1985 to 1988

Meteorological station (test site)	Temperature/ °C (Min. - Max.)	TOW / h.y ⁻¹ (% of max. possible)	Precipitation / mm.y ⁻¹
Roca (Roca)	15.4 (9.1 - 23.1)	5028 (58%)	491
Lavradio (Barreiro)	14.8 (5.9 - 29.4)	3388 (39%)	620 ^a
Lisbon (LNEC)	16.6 (6.7 - 29.1)	3315 (38%)	723
P. Rocha (Alfanzina)	14.5 (8.3 - 28.2)	1683 (21%)	518

^a1985/87

During the 10 years of exposure, several visual inspections have been made, especially in the first years. Triplicate specimens for corrosion evaluation plus one for reference were taken after 6 months, 1, 3, 5 and 10 years of exposure.

Evaluation of results

The evaluation of results for the first periods of exposition was done some time after its collection from the test sites. During this time, the test specimens were kept stored in closed plastic bags away from light, in a dry place.

Visual appearance

All the specimens were subjected to visual inspection for assessment of surface condition. During the exposure a general darkening took place, more rapidly in the industrial site Barreiro, where the colour of the copper surface changed to a very dark brown only after 6 months. In the marine atmos-

pheres, Roca and Alfanzina, during the first year, the copper surfaces acquired a reddish appearance which lately has turned into a reddish brown. On these sites the formation of green stains (more intense at Roca) has been observed since the beginning of the exposure. On the urban site, Lisbon, the darkening process was slower, the colour of the copper surface has gradually changed from a glossy orange to a reddish brown, matte. The observed aspects of the upper surfaces of the test specimens, after 10 years of exposure, are reported in Table 4.

Table 4 – Surface appearance of copper test specimens after 10 years of exposure

Site	Aspect
Roca	<i>Marine</i> Sparse bluish green on very dark red, smooth
Barreiro	<i>Mar.-indus.</i> Brownish black with green spots, very rough
Lisboa	<i>Urban</i> Reddish brown, smooth
Alfanzina	<i>Marine</i> Reddish brown, sparse green stains, smooth

Corrosion evaluation by weight loss

Copper corrosion behaviour was evaluated by weight loss. A cleaning procedure for removal of corrosion products, according to ISO 8407, was used: immersion in a solution of chlorhydric acid (500 ml) in distilled water to make 1000 ml, at ambient temperature, for 2 minutes. Rinse in distilled water.

The cleaning procedures were repeated in equal cycles whenever it was necessary until the samples were all free from corrosion products. After cleaning, test specimens were reweighed to the nearest 0.01g. The results, averaged from triplicate specimens are given in Fig.1.

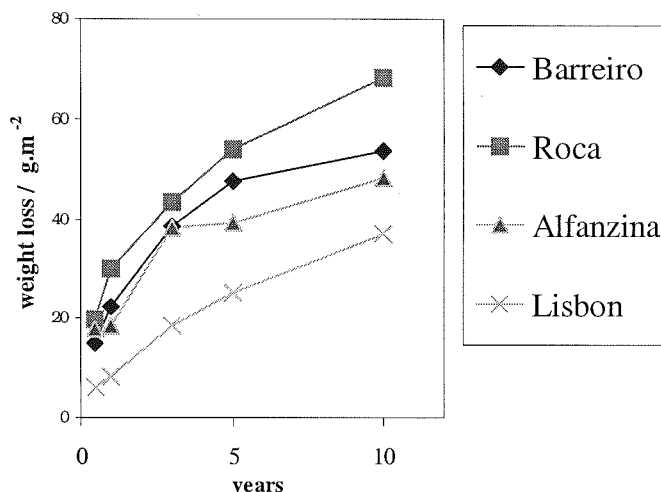


Fig. 1 – Corrosion of copper after 6 months, 1, 3, 5 and 10 years of exposure.

Composition of copper corrosion products

Corrosion product samples were scrapped from the topside

of the copper test specimens. The mineralogical composition of the corrosion products formed after 6 months, 5 and 10 years of exposure was determined by X-Ray diffraction analysis (XRD) for some test sites. The results obtained, in several samples, are given in Table 5.

In addition to XRD analysis the surfaces of the specimens were observed by scanning electron microscope (SEM) equipped with an energy dispersive X-Ray spectrometer (EDS) to determine the elemental composition of the corrosion products layer. These results obtained for 10, 5 and 6 months of exposure are presented in the Fig.2.

Table 5 – XRD analysis of corrosion layers

Site	Barreiro			Roca Alfanz.	Lisbon		
	0.5	5	10	10	0.5	5	10
<i>time (years)</i>							
Cu ₇ Cl ₄ (OH) ₁₀ .H ₂ O	*	*	*	*			*
Cu ₂ O	**	**	**	**	**	**	**
CuCl	*	*				*	
Cu ₂ Cl(OH) ₃						t	
Cu ₄ SO ₄ (OH) ₆						*	*
Cu ₄ SO ₄ (OH) ₆ .H ₂ O					t		
Fe ₂ O ₃ , FeS ₂					*	*	*
SiO ₂	t	t	*	t	t	t	
CaCO ₃	*				*	*	
CaSO ₄ .2H ₂ O	t	t			t	t	

** more predominant; * less predominant; t – traces

The copper oxide *cuprite* is the main constituent of the corrosion layers. The iron compounds found at Barreiro result from the deposition of airborne particles of iron compounds coming from open-air deposits of pyrites or from emissions of the siderurgy nearby.

Composition of corrosion products (patina) of bronze and brass statues

Samples were collected on the *patina* of statues from six monuments inspected, between 1996 and 1998, for corrosion diagnosis. The chemical analyses by SEM-EDS and X-Ray diffraction were done on these samples. Table 6 presents the main constituents of the patinas, identified by XRD analysis.

Table 6 – XRD analysis of patina composition (main compounds) of bronze/brass statues exposed in different locations with ages from 30 to 200 years

environment	urban-marine		urban	
	brass	brass	brass	bronze
Cu ₄ SO ₄ (OH) ₆			**	**
Cu ₇ Cl ₄ (OH) ₁₀ .H ₂ O	**		t	t
Cu ₂ O	*		*	*
CuCl	*		*/t	*/t
Cu ₂ Cl(OH) ₃	*		*	*
CuSn(OH) ₆ ¹⁾			**	
SiO ₂	*		*	*

** more predominant; * less predominant; t – traces

¹⁾only in the oldest case

On the surface of the bronze and brass statues with decades of atmospheric exposition, predominate products formed as the result of the aggressive action of atmospheric gaseous pollutants SO_2 or chloride ions, like the basic sulphate *brochantite* ($Cu_4SO_4(OH)_6$) and the basic chloride hydrate $Cu_7Cl_4(OH)_{10} \cdot H_2O$, with only some oxide *cuprite* (Cu_2O).

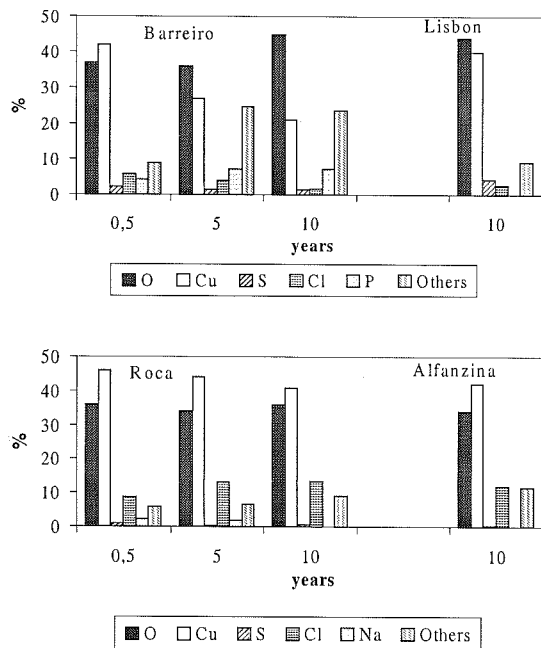


Fig. 2 – SEM-EDS elemental semi-quantitative analysis of corrosion products layer for copper test specimens. Other elements detected were: Ca, Si, Al, Mg, Fe and Zn.

Copper corrosion behaviour as a function of time

In general the weight loss values show a tendency to be proportional to the time of exposure or to exhibit slower increases with time. This behaviour is often represented by an expression of the following type [3]:

$$M = Kt^n \quad (1)$$

where:

- M is the total weight loss caused by corrosion per unit of exposed area, $g \cdot m^{-2}$;
- K is a proportionality constant, expresses the weight loss occurring in the first year;
- n is the weight loss exponent;
- t is the exposure time, years.

Values of n smaller than 1 indicate reduction of the corrosion rates with time, characteristic of a system with a uniform protective corrosion product layer. The smaller the

weight loss exponent, the more protective the coating and the better the long-run performance of the alloy. Copper alloys, however, not always follow this kinetics [3].

In order to calculate the constants K and n in Eq.1 from the weight loss data (Fig.1), a linearization by logarithmic conversion was done so as to use the simple least square regression analysis. The calculated values of K , n and R are given in Table 7.

Table 7 - Results of regression analysis of weight loss with exposure time

Site	n	K	r
Barreiro	0.44	22	0.97
Roca	0.40	28	0.99
Alfanzina	0.37	22	0.97
Lisboa	0.62	9.0	1.00

Influence of Sulphur Dioxide and of Chloride atmospheric contamination

Chlorides and nowadays, sulphur compounds, especially sulphur dioxide (SO_2), constitute the most important aggressive agents in atmospheric corrosion. In order to evaluate the correlation between the corrosion rate of copper on each test site and the content of sulphur dioxide and chlorides in the atmosphere, a multilinear regression analysis was performed by the least squares method based on the following equation:

$$CR = aSO_2 + bCl + c \quad (2)$$

where:

- CR is the corrosion rate, in $mm \cdot y^{-1}$, for a given time of exposure;
- SO_2 and Cl are the correspondent average deposition rates, in $mg \cdot m^{-2} \cdot y^{-1}$, for the same time of exposure.

Table 8 – Copper corrosion rates after 1 and 10 year exposures

Site	Corrosion rates / $\mu m \cdot y^{-1}$	
	1 year	10 years
Barreiro	2.5	0.6
Roca	3.4	0.8
Alfanzina	2.1	0.5
Lisbon	0.9	0.4

Eq.2 was applied to data from one year and ten years of exposure, considering that SO_2 and chloride deposition rates

average values do not change from eight years to ten years of exposure. Tables 8 and 9 present the corrosion rates, as well as the pollution data for 1 and 10 years of exposure. The results of the regression analysis for the application of equation (2) are presented in Table 10.

Table 9 - SO₂ and Chloride average deposition rates after 1 and 10 years

Site	SO ₂ / mg.m ⁻² .y ⁻¹		Cl ⁻ / mg.m ⁻² .y ⁻¹	
	1 year	10 years	1 year	10 years
Barreiro	220	136	41	38
Roca	5	6	132	194
Alfanzina	5	8	56	201
Lisbon	14	14	2	7

Table 10 – Least squares coefficients for Eq.2

	1 year	10 years
<i>a</i>	0.0037	0.001
<i>b</i>	0.019	0.001
<i>c</i>	0.9	0.4
<i>r</i>	1.00	0.76

Results interpretation and conclusions

- The weight losses of copper specimens were significantly higher at the marine and industrial sites than at the urban site, reflecting a relative low level of atmospheric contamination in Lisbon (*urban*). The most severe site was Roca (*marine very wet*). The corrosion rates after one year of exposure were 0.9 mm/y in Lisbon and ranged from 2.1 mm/y to 3.4 mm/y on the other sites. After ten years, the corrosion rates at the four sites were much lower and closer: 0.4 mm/y at Lisbon (*urban*), 0.5 mm/y and 0.8 mm/y at the *marine* sites and 0.6 mm/y at the *industrial-marine* site. The reason for this decrease is the formation of uniform protective layers of copper oxide *cuprite* (identified by XRD analysis) in all specimens. The values of corrosion rates are close to those obtained in similar studies[4,5] for the marine sites, but lower for the urban and industrial-marine exposures.

- The corrosion products formed on copper during exposure are constituted mainly by copper oxide *cuprite* and some basic chlorides for all sites and also some basic sulphate *brochantite* for the urban site. These two basic copper salts are the most commonly found in statues of copper alloys exposed to urban-marine and urban atmospheres, respectively. The reason for their appearance in small quantities in the copper test specimens should be the relatively short time of exposure of this study. Ten years seems to be insufficient for the development of basic copper salts in larger amounts.

- By the analysis to the composition of the corrosion products formed on the copper test specimens, the most surprising feature

is the absence of corrosion products with sulphur at Barreiro (*industrial-marine*) in spite of the higher values of SO₂ atmospheric pollution of this site, specially in the first years of exposure. Neither any copper sulphate was identified by XRD analysis (Table 5), nor significant levels of sulphur were detected by SEM-EDS analysis (Fig.2) of the corrosion layers. One possible reason for this could be the formation of only high soluble copper sulphates. Other possible explanation is the fact that the presence of significant levels of phosphorus (detected by SEM-EDS, Fig.2) on the surface of the copper test specimens from this site, (possibly as the result of deposition of airborne phosphate particles from the fertiliser production plant nearby), could in some way have inhibited the formation of copper sulphates. This inhibition action could also justify the relative low corrosion rates verified on this site as an industrial atmosphere, when compared with other studies[4,5]. Despite of the absence of sulphate copper corrosion products, the presence of SO₂ in the atmosphere of Barreiro should have had some responsibility in the acceleration of the corrosion rate, which is similar to the values obtained for the marine sites.

- The weight loss evolution in time agreed well with the kinetic law $M=Kt^n$. The weight loss exponent values smaller than one, once more indicate the formation of protective corrosion layers and that the corrosion rates should be stabilising.

- The correlation between SO₂ and chloride atmospheric concentration and the corrosion rate of copper using eq.2 yielded good agreement for the initial values (one year of exposure). However, the same does not apply to the ten-year results. This is due to the formation of protective corrosion layers, which reduce the corrosion rate. The lower corrosion rates of copper and copper alloys due to the formation of protective corrosion layers is the main reason for the good environment stability of bronze and brass statues.

References

- [1] Cravo, M. R., "Estudo da corrosão atmosférica de metais e revestimentos inorgânicos utilizáveis em coberturas e caixilharias – 2º Relatório-Characterização de materiais e detecção de poluentes atmosféricos agressivos", LNEC Report, Lisbon, 1980
- [2] Salta, M.; Fontinha, I. R., "Corrosão em estátuas metálicas", 8th National Meeting of the Portuguese Materials Society – MATERIALS'97, vol.2, June, 1997, 300-306
- [3] Dean, S. W., "Corrosion testing of metals under natural atmospheric conditions", STP 1000, ASTM, Baboian R. and S. W. Dean, Eds., 1990, 163-176
- [4] Holm, R.; Mattsson, E., "Atmospheric corrosion tests of copper and copper alloys in Sweden- 16 years results", STP 767, ASTM, S. W. Dean, Jr. and E. C. Rhea, Eds., 1982, 85-105
- [5] Costas, L. P., "Atmospheric corrosion of copper alloys exposed for 15 to 20 years", STP 767, ASTM, S. W. Dean, Jr. and E. C. Rhea, Eds., 1982, 106-115