The Initial Stages of the Atmospheric Corrosion of Copper at an urban Atmosphere

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Abstract

Studies on the initial stages of the atmospheric corrosion of copper exposed to the urban atmosphere of the city of Lisboa, at a site called Campo Grande, from November 2000 till February 2001 (winter period), are presented in this paper.

Average corrosion rates of 0.139 and 0.105 g m^{-2} day^{-1} were obtained for copper samples after one and three months of exposure, respectively.

From SEM/EDS data it was concluded that during the first month of exposure corrosion products were mainly composed by copper oxides and minor amounts of copper chlorides, while exposures of two and three months lead to the formation of copper sulphates apart from copper oxides and copper chlorides. A uniform and adherent film was visible on the surface after three months of exposure.

During the period under evaluation concentrations of NO_2 were between 32 and 36 ppb and deposition rates of SO_2 between 17 and 20 mg m^{-2} day^{-1}, without significant changes during the three-month period. The degree of humidity and the average precipitation were both quite high (winter season). The SO_2 present in the atmosphere with a high degree of humidity explains the formation of copper sulphates.

Keywords: Atmospheric corrosion; Copper; Urban atmosphere; Patinas.

Resultados de um estudo sobre a fase inicial da corrosão atmosférica de amostras de cobre expostas na atmosfera urbana da cidade de Lisboa, no local designado de Campo Grande, durante o período de Novembro de 2000 a Fevereiro de 2001 (estação de Inverno), são apresentados.

Valores de velocidades médias de corrosão de 0.139 e 0.105 g m^{-2} d^{-1} foram obtidos após um e três meses de exposição, respectivamente.

Estudos de SEM/EDS revelaram filmes não uniformes compostos predominantemente por óxidos de cobre e em menor percentagem cloretos, em amostras com menos de um mês de exposição, enquanto, após o segundo mês de exposição se observou um filme uniforme constituido por sulfatos além de óxidos e de cloretos de cobre.

Os níveis médios de NO_2 no período em estudo situaram-se entre 32 e 36 ppb e as taxas de deposição do SO_2 entre 17 e 20 mg m^{-2} d^{-1}, sem variações significativas durante o período em análise. Os graus de humidade e pluviosidade foram em geral elevados durante todo o trimestre em análise (estação de Inverno).

A presença de sulfatos nas patinas deve-se, naturalmente, aos níveis de SO_2 presentes numa atmosfera com um grau de humidade bastante elevado, durante o período em análise.

Palavras chave: Corrosão atmosférica; Cobre; Atmosfera urbana; Patinas.

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Introduction

The formation of patinas on copper upon exposure to the atmosphere is perhaps the most common evidence of the interaction of atmospheric trace substances with metal surfaces.

Copper when exposed to an urban atmosphere becomes covered with a greenish-blue patina: a protective and decorative film. During the initial period of exposure this thin film develops before the formation of the passive films. The initial process depends on several parameters, namely on the climatic factors (temperature, pluviosity and humidity). The composition of the surrounding atmosphere (degree of contamination by aggressive gases), as well as the characteristics of the material (structure, degree of rugosity, impurities, etc.) are important factors to take into account in the whole process. Constituents of natural copper patinas are those compounds thermodynamically stable under atmospheric exposure [1].

Several groups over the world have undertaken studies on the atmospheric corrosion of copper and copper alloys, outdoor and also indoor exposures, in closed spaces or laboratory tests, under controlled conditions (chambers of SO_2, CO_2, humidity, etc.) [2-9]. The topic remains an interesting topic of research, since atmospheric corrosion depends on a great variety of parameters, namely on climatic parameters and level of pollutants in the atmosphere. Since great climatic changes are occurring all over the world then actual data may be very different from previous one, even for the same local and same season. Corrosion rates and the nature of corrosion products depend on the climate changes and also on the degree of pollution of a given city or local.

From previous studies on the atmospheric corrosion of copper samples also exposed to the atmosphere of the city of Lisboa, from November 1999 till August 2000, it was concluded that it would be important to collect and analyse data during the initial stages of the exposure [10].

On a very recent paper Aastrup *et al* [8] have studied the influence of humidity, sulphur dioxide, ozone, and nitrogen dioxide on the initial atmospheric corrosion of copper samples.

Experimental

Copper samples were cutted from copper sheets containing 0.024 % of P. Samples of 15x10 cm were prepared for exposure (duplicates for weight loss measurements and singles for surface analysis).

All copper samples were first polished with emery paper grid number one and number zero then, washed several times with distilled water and finally degreased with acetone. Samples for weight loss determinations were weighted before and after exposures. After exposure, corrosion products were removed by immersion, during 45 seconds, in a solution made of sulphuric acid and potassium dichromate (ISO/DIS 28407.3), then samples were washed several times with distilled water, degreased and dried with acetone, before being re-weighted.

An essay station made of a panel of dexion was mounted, at the terrace of building designated as C1, in the Faculty of Science of the University of Lisboa, at Campo Grande (a place near roads of intense traffic but also sided by a quite large green park). The co-ordinates of the essay site are latitude - 38° 45´ 38´´ N, longitude - 9° 9´ 42´´ W and altitude -100 m ellipsoidal.

The period of this study is from November 2000 till August 2001. However data presented in this paper covers only the initial 3 months of exposure.

The scanning electron micrographs and SEM/EDS data were obtained with a scanning electronic microscope, JEOL JSM-35 CF, equipped with an energy dispersive diffractometer.

Results

Corrosion rates

Corrosion rates obtained from weight loss measurements are plotted in the graph of Fig.1. (a) The average corrosion rate starts with a value of 0.139 g m^{-2} day^{-1}, after one month of exposure, and slows down to 0.105 g m^{-2} d^{-1} after three months of exposure.

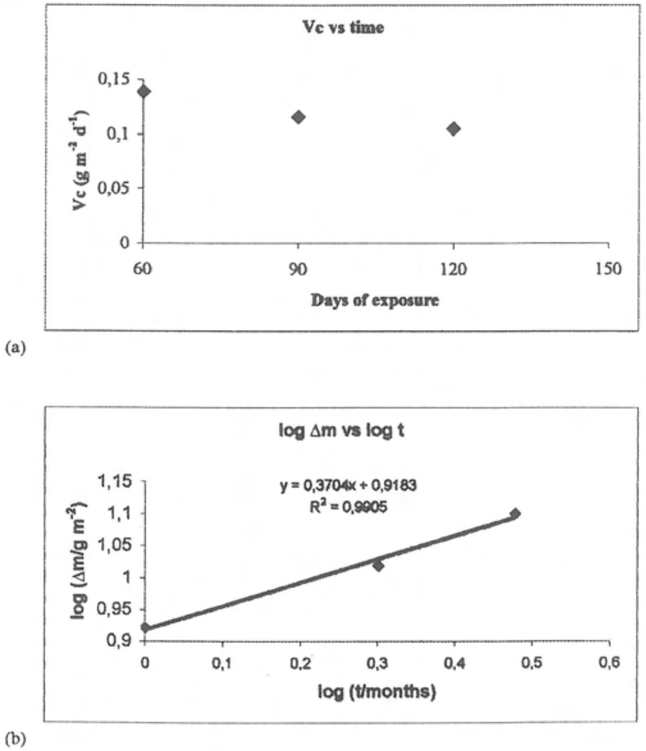

Fig. 1 (a) Average corrosion rates of copper samples as a function of exposure time
(b) Log-log plot of weight loss *vs* exposure time.

The average corrosion rates after two months of exposure are of the same order as those obtained by Ramos [10], at the same site, from November 1999 till January 2000.

From data of Fig. 1. (b) an equation for the corrosion kinetics may be proposed, i.e. equation (1)

$$\Delta m = k\, t^{0.4} \qquad (1)$$

With k= 8.28 g m^{-2} $month^{-0.4}$. The smaller the weight loss exponent, the more protective the film and therefore the better the long-term performance of the sample. Values ranging between 0.15 and 1.0 have been obtained for the exponent of eq. (1), from studies with copper samples exposed for a period of 8 years, in an urban/industrial atmosphere, in the city of Barcelona, in Spain [9].

Visual inspection

Photographs of copper samples with one, two, three and four weeks and two and three months of exposure are given in Fig.2 (a) and (b)

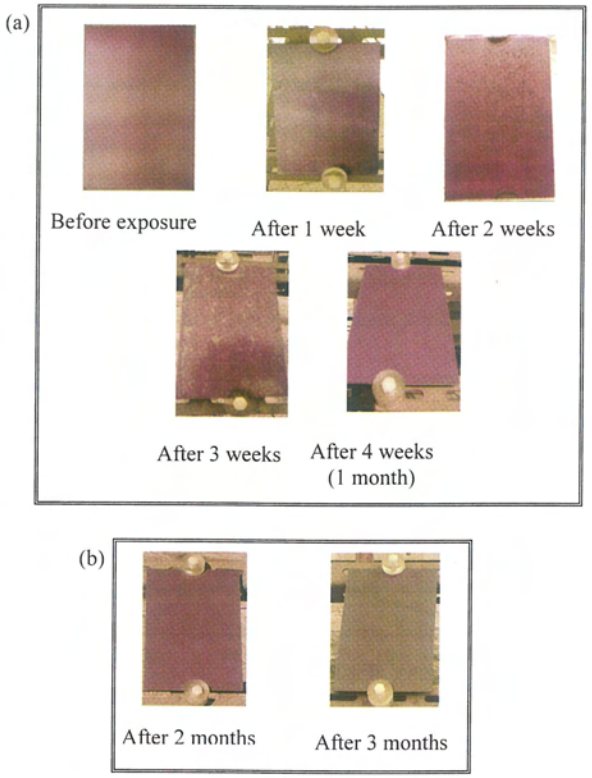

Fig.2.Photographs of copper samples with the following exposure times:
(a) 1 month; (b) 2 and 3 months.

The morphology of the copper samples exposed during three weeks show large areas of corrosion products with a reddish-brown colour and small blue–white coloured areas. Samples with four weeks of exposure show a smooth and uniform film, keeping the reddish-brown colour. Films corresponding to exposures of two and three months are still quite uniform and with good adherence. Their colour turns into a more brownish one.

SEM/EDS Studies

Scanning electron micrographs of copper samples with one and four weeks and also of two and three months of exposure with different magnifications are presented in Fig.3 and Fig.4. Difractograms of selected zones indicated in the micrographs are also given in figures 3 and 4.

The micrographs on Fig.3 (a_1) corresponding to an amplification of 350x show the general pattern of the surface at a microscopic level. Black spots distributed over the whole surface are visible. Elements identified by EDS, on these samples, were Cl and O apart from Cu. Micrographs presented in Fig.3 (a_3) corresponding to 4 weeks of exposure show black spots of larger size and an increase in the amount of corrosion products. An amplification of 2500x shows the shape and morphology of the corrosion products. Elements identified were Cl, O and a very little amount of S, apart from Cu.

On Fig.4 (a_1) the images show a surface with a more uniform pattern. Micrograph (a_2) shows a big "hole". On Fig.4 (a_3) the micrograph with a magnification of 35x shows a uniform film covering the entire surface. A higher amplification shows the morphology of the corrosion products (micrographs a_2 and a_4).

The EDS spectrum (b_3), (b_4) and (b_5) show peaks correspondent to Cu, Cl, O and S. Elements identified by EDS are given in Table 1. The EDS was not able to detect nitrogen, therefore, nitrates, if present in the corrosion products, they could not be identified by EDS. On the other hand, it is well known that copper nitrate compounds, such as the gerhardite, are stable only at very high nitrate concentrations.

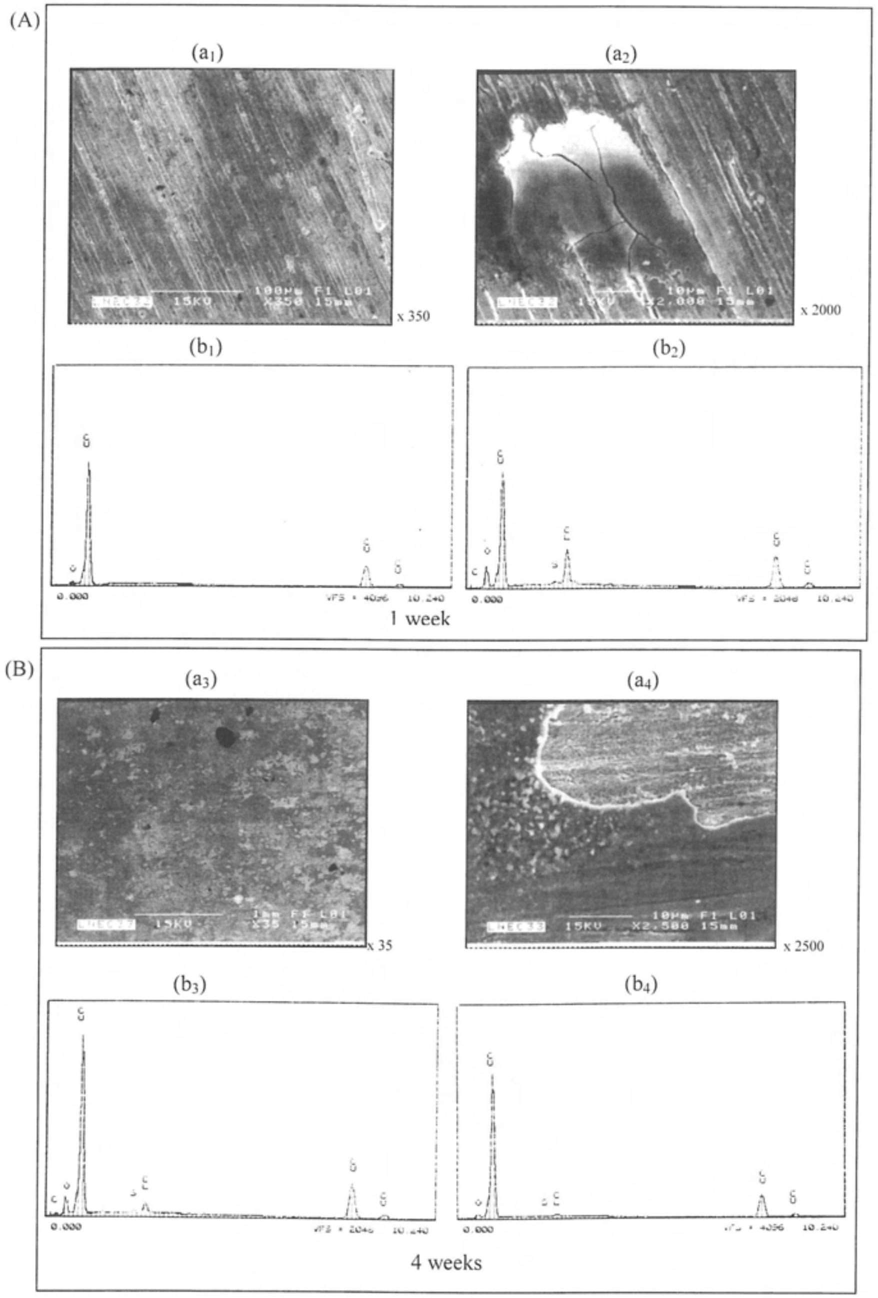

Fig.3. SEM micrographs and EDS spectra of copper samples after:
(A) 1 week; (B) 4 weeks of exposure.

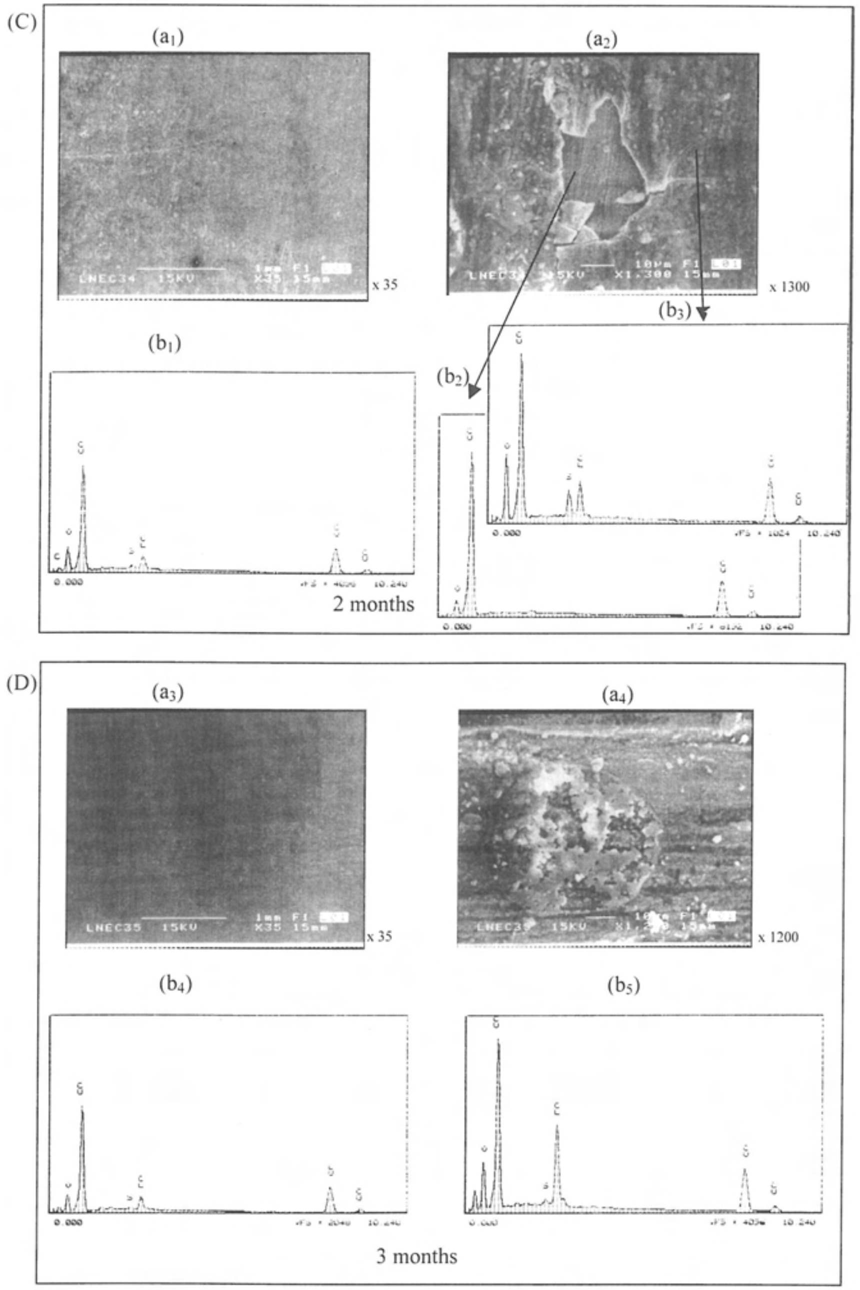

Fig.4. SEM micrographs and EDS spectra of copper samples after:
(C) 2 months and (D) 3 months of exposure.

Table 1 Elements identified by EDS .

Exposure time	Elements identified by EDS	Possible compounds
1 week	Cu, Cl and O	Cu_2O (cuprite), CuO (tenorite), CuCl (nantokite), Cu_2Cl (tolbacite), $Cu_2Cl\ (OH)_3$, (atacamite).
4 weeks (1 month)	Cu, Cl and O	Cu_2O (cuprite), CuO (tenorite), CuCl (nantokite), Cu_2Cl (tolbacite), $Cu_2Cl\ (OH)_3$, (atacamite).
2 months	Cu, Cl, O and S	Cu_2O (cuprite), CuO (tenorite), CuCl (nantokite), Cu_2Cl (tolbacite), $Cu_2Cl\ (OH)_3$, (atacamite), $CuSO_4.2Cu(OH)_2$ (antlerite), $CuSO_4\ .3Cu(OH)_2$ (brochantite).
3 months	Cu, Cl, O and S	Cu_2O (cuprite), CuO (tenorite), CuCl (nantokite),Cu_2Cl (tolbacite), $Cu_2Cl\ (OH)_3$, (atacamite), $CuSO_4.2Cu(OH)_2$ (antlerite), $CuSO_4\ .3Cu(OH)_2$ (brochantite).

Accordingly to the Pourbaix diagrams for Cu-S-Cl-H_2O [11] possible corrosion products are Cu2O (brown); CuO (reddish-dark); CuSO4 3Cu (OH) 2 (blue); Cu2Cl (OH) 3 (white); and CuCl (white).

Crystalline compounds may be identified by X-rays analysis. Salts of organic acids as well as other inorganic salts may also be present in the corrosion products. Ionic chromatography analysis of the corrosion products may be able to detect this type of compounds even when present at very low levels.

The most significative difference in the patinas´constituents, given by the EDS spectra, is the presence of copper sulphates on samples with periods of exposures longer than two months (see data on Table 1.).

Atmospheric Data

Levels of SO_2 and of NO_2 measured from air samples collected at the same local where copper samples were exposed for the period under evaluation are presented in Table 2. Climatic data collected from the web site www.meteo.pt is also given in Table 2.

Table 2. Monthly average values of SO_2, NO_2 and meteorological data for the atmosphere of Campo Grande, from November 2000 until January 2001.

Period	SO_2 ($mg\ m^{-2}\ day^{-1}$)	NO_2 (ppb)	Precipitation N° of days /month	Wind direction (Degrees)	Average Relative humidity %
November 2000	17	35	14	218	80
December 2000	16	36	24	211	85
January 2001	20	32	19	235	84

During the period under analysis the levels of NO_2 and of SO_2 in the atmosphere have not changed significantly. The decrease in the corrosion rates and/or the evolution of patinas´composition cannot be attributed to the changes of the levels of pollutants during the three-month period. However the formation of sulphates is naturally related with the presence of SO_2 in an atmosphere with a high degree of humidity (RH ≥ 80 %). Also the presence of copper chlorides in the copper patinas is due to sea-salts transported by the winds dominating most of the time from the Atlantic side.

The non-uniform morphology of the corrosion products during the initial stages of the exposures, is related with the high intensity of the winds during most of this period, and to the high levels of precipitation: 14, 24 and 19 days, in November, December and January, respectively.

Conclusions

- Average corrosion rates of copper samples exposed to the atmosphere of the city of Lisboa start with a value of 0.139 $g\ m^{-2}\ day^{-1}$, after one month and slow down to 0.105 $g\ m^{-2}\ day^{-1}$ after three months of exposure.
- Copper samples with a few weeks of exposure show a non-uniform film. However, after three months of exposure the film becomes quite uniform. Even when observed at microscopic level the uniformity was kept as shown by the scanning electron micrographs.
- EDS spectra show Cu, O and Cl as the principal elements of the corrosion products formed during the first three weeks of exposure. During the fourth week compounds containing S are certainly formed since S was identified by EDS. Thereafter, the amount of sulphates on the patinas increases.
- The composition of the patinas can be predicted from Pourbaix-diagram with the elements identified by EDS and the colour of the corrosion products: copper oxides (cuprite and tenorite)

and copper chlorides (nantokite and/or tolbacite) on samples with three weeks of exposure. Copper sulphates (antlerite and/or brochantite), apart from copper oxides and copper chlorides, on copper samples with more then 4 weeks of exposure.

- The presence of copper sulphates among the patinas´constituents is related with the high levels of SO_2 in a highly humid atmosphere (winter season).
- The presence of copper chlorides among the corrosion products is related with the strong winds blowing most of the time from the Atlantic Ocean (SW).
- The high levels of precipitation combined with the strong winds explain the non-uniformity of the corrosion films formed during the initial stages (rain-washes corrosion products).
- Nitrates may also be present in the corrosion products but SEM/EDS does not detect nitrogen. On the other hand, the stability diagram of the copper-nitrate-water system shows that copper nitrate compounds are stable only at very high nitrate concentrations, and that may not be the case.

In order to separate the influence of exposure time and atmospheric parameters (contaminants and climatic ones) exposures of samples with delays of one month in relation to the first day of the test are planned.

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