

Copper corrosion in soil: influence of chloride contents, aeration and humidity

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Abstract The corrosion of copper in a typical Portuguese soil was studied. The original soil was characterised, and modifications were produced by adding chloride, and HClO₄ solutions, or by increasing its relative humidity. The aggressiveness degree of the various soil samples was determined. Copper coupons exposed for 3 months in the original and in the modified soil samples were analysed. The average corrosion rates determined from gravimetric data were in good correlation with the soil aggressiveness. The morphology of the corroded copper surfaces, with and without corrosion products, was analysed by visual observation, optical microscopy and scanning electron microscopy. Energy dispersive spectroscopy was used for the semi-quantitative analysis of the corrosion products and X-ray diffraction spectroscopy to identify the crystalline

products. Cuprite has been identified on the copper samples corresponding to the interfaces Cu|S6 and Cu|S8, plus paratacamite on the copper coupon exposed to the soil with higher concentration of chloride (S6). Polarisation curves of copper samples in neutral solutions made by adding different amounts of chloride ions to the soil washing water, under deaerated conditions, were recorded and analysed. The passivity breakdown potential has shown, as expected, a displacement to the cathodic direction as the Cl⁻ ion concentration increases.

Keywords Copper corrosion · Soil aggressiveness · Steinrath index · Soaked soil · Passivity breakdown potential

Introduction

The influence of the soil composition on the corrosion resistance of buried metallic structures and the nature of the corrosion products formed are of great importance in many industrial applications, as well as in archaeological studies of metallic finds [1–4]. Modifications in the soils characteristics can result from agricultural activity, such as fertilisation, chemicals accidentally spilled into the soil (acids or strong bases), acid rains, etc.

The soil texture can also influence its aggressiveness since the drainage and aeration are texture-dependent. Gerwin and Baumhauer [4] concluded that corrosion of buried iron objects often decreases in loamy soils because of oxygen deficiency. On the other hand, a sandy soil results in comparatively good drainage and aeration. Corrosion of most metals in soils is controlled by diffusion of the dissolved oxygen [5].

Lopez et al. [6] concluded that soils having high moisture contents, high dissolved salt concentration and

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high acidity are in general more aggressive; however, at least for short-term exposures soil composition alone has been found to have little correlation with soil corrosivity. Most probably, only long-term exposures with high residence time of water or moisture on the metal surface will corrode to a high extent, particularly when the metallic specimens are immersed in aerated water.

Srivastava and Balasubramaniam [7] examined copper samples exposed to different soil environments, namely soils containing chloride, sulphide and ammonium salts. The damaging effects of chloride ions and the role of sulphide ions were determined.

Kvashnina et al. [8] analysed by in situ X-ray absorption spectroscopy the modifications induced on the copper films by chemical reactions with chlorides and/or HCO_3^- in aqueous medium. They concluded that the corrosion of copper can be significantly reduced by adding small amounts of sodium bicarbonate. It was also observed that copper films corroded quickly in chloride solutions, whereas the same solution containing 1.1 mM HCO_3^- prevented or slowed down the corrosion process.

The influence of chloride ions on the corrosion of copper in aqueous solutions, under various experimental conditions, has been extensively studied by Ferreira et al. [9] and Kear et al. [10] and references therein.

Corrosion of copper and copper alloys in soils and in ground waters is in general controlled by the availability of oxygen, but the final corrosion products will be controlled by the composition of the ground water contacting the copper surface. In general, copper corrosion in ground waters or soils leads to corrosion products, such as cuprous chloride, CuCl , cupric chloride, CuCl_2 , basic copper chlorides, e.g. paratacamite, $\text{Cu}_2(\text{OH})_3\text{Cl}$, or atacamite, $\text{Cu}_2\text{Cl}(\text{OH})_3$, both light green, cuprous oxide, Cu_2O , brown reddish and the green and blue-coloured cupric carbonates, malachite, $\text{Cu}_2\text{CO}_3(\text{OH})_2$ and azurite, $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$, respectively and copper sulphates such as brochantite [11–13].

The most damaging effect occurs in high chloride concentrations and, in such conditions, basic cupric chlorides such as paratacamite and atacamite may form. Ribotta et al. [14] have noticed a decrease in the amounts of Cu (II) species as a consequence of the pH buffering by HCO_3^- which stabilises the oxide film rather than leading to the formation of basic cupric carbonate species.

In spite of the reported studies on the copper corrosion in soils, there is still a lack of information and many aspects

need to be elucidated. It is also desirable to find a correlation between the degree of aggressivity of the soils, such as the ones given by the Steinrath index [15] and the corrosion rates obtained from gravimetric experiments. Then, it will be possible to predict long-term corrosion susceptibility based on the soil aggressivity. On the other hand, pitting corrosion can be predicted from the passivity breakdown potentials, E_b , obtained from the quasi-steady state polarisation curves.

Experimental

A fraction of the soil collected in a suburban area of Sintra, in Portugal, was dried at 105 °C for ca. 24 h and then left in the desiccator. Soil sampling and analysis were performed following the procedures described elsewhere [16, 17].

The soil redox potential was determined with a Pt electrode immersed in a water-saturated soil sample following the procedure described elsewhere [16, 17]. The Pt electrode was connected to a commercial saturated calomel electrode through a salt bridge. Measurements were taken every 5 min, for about 30 min, with a digital multimeter Fluke 8600A.

Soil resistivity (ρ) measurements were conducted with a Philips cell following the ASTM ST74 [18]. The soil suspension was prepared with one part of soil and two parts of distilled water. An Impedance Meter model 253, from ELECTRO SCIENTIFIC INDUSTRIES, Portland, Oregon, USA was used. The pH measurements were performed following standard methods [19], using a portable pH Meter model PHM210 from Radiometer Analytical.

Table 1 gives the concentrations of the elements that have been analysed in the original soil sample (S1). Other elements are certainly present but they are of minor importance for this study. The soil pH, resistivity and redox potential are also given in Table 1.

The original soil sample (S1) was modified by adding calculated amounts of KCl or HClO_4 . The procedure used in the preparation of the modified soil samples and its identification is given in Table 2.

The volume of 130 mL of water or modifier solution added to the weighted dried soil was calculated in order to give a relative humidity (RH) of 60% (samples S1, S3–S8). Sample S2 (soil soaked with water) is considered as having an RH of 100%.

Table 1 Data from soil analysis

Fe (mg kg ⁻¹)	Cu	Zn	Mn	P	K	SO_4^{2-}	Cl^-	pH	E_{redox} (V vs. SCE)	ρ (k Ω cm)
128	7	2	282	37	59	190	17	7.9	-0.28	2.9

Table 2 Composition of the various soil samples

Soil sample	Mass of dried soil (g)	Volume of the modifier solution (mL)	Composition of the modifier solution
S1	710	230	Distilled water
S2	406	Water to cover the soil (0.5 cm)	Distilled water
S3	400	130	0.18 mL of KCl 0.5 M
S4	400	130	0.87 mL of KCl 0.5 M
S5	400	130	3.04 mL of KCl 0.5 M
S6	400	130	3.9 g of KCl in 130 mL
S7	400	130	10 mL of HClO ₄ 1 M
S8	400	130	20 mL of HClO ₄ 1 M

Copper coupons (99.92% Cu + 0.024% P) of 2 cm × 8 cm, were polished firstly with emery paper of grade sizes 400 and 1,000, and secondly with 1 μm alumina powder, washed with water and acetone and finally dried, labelled and weighted. Then, they were placed in the vertical position fully buried in the soil samples, two replicas of copper coupons for each soil sample and a third copper coupon two-thirds buried in the soil sample S1.

The beakers containing the copper coupons buried in the respective soil samples were sealed in order to keep the degree of humidity (checked by weighting them periodically). The soil S2 (beaker 2) was fully covered with distilled water (RH=100%). After a 3-month period, the copper coupons were removed from the respective soil sample. Again, they were weighted after the removal of the corrosion products following the methodology given in the ASTM standards [20]. The cleaning process was repeated until a constant weight was obtained. A KERN 770 balance was used.

Soil solutions for the electrochemical studies have been prepared by washing 50 mg of dried soil with 500 mL of distilled water, at 50 °C, under stirring conditions for 24 h. Then, the solution was left to settle down for another 24 h and finally filtered one or more times, when necessary, with filters of low porosity.

The filtered solution will be referred as ‘soil washing solution’. For the electrochemical studies, NaClO₄ 1 M was added to the aqueous solution to avoid ohmic drop, as well as different amounts of NaCl, in order to vary the levels of chlorides, from the blank (17 ppm) to 0.5 mol dm⁻³.

A three-electrode cell with a platinum grid as counter electrode and a commercial saturated calomel electrode (SCE) as reference electrode were used. The cell was filled with the corresponding solutions that were deaerated by nitrogen bubbling, during ca. 20 min, before the electrochemical tests. The working electrode (area 0.2 cm²) was polished after each polarisation. Polarisation curves were

obtained via an AUTOLAB[®] PGSTAT12/General Purpose Electrochemical System from Eco Chemie B.V. (The Netherlands). All experiments were conducted keeping the electrochemical cell inside a Faraday cage.

The scanning electron microscopy (SEM) and the energy dispersive spectroscopy (EDS) studies were performed using a scanning electron microscope JEOL 6700 coupled to an OXFORD EDS system.

X-ray diffractograms were obtained with a Philips PW 1710 diffractometer equipped with a graphite monochromator coupled to a vertical goniometer (PW 1820). The X-ray source (Cu-Kα radiation) was operated at 30 mA and 40 kV, with automatic data acquisition (APD Philips software v. 3.6B). Diffractograms were obtained in the 2θ range of 10.00° to 90.00°, at a scan rate of 0.02° s⁻¹.

Results and discussion

Soil characterisation

The aggressivity of soil samples was classified by calculating the total Steinrath index [15] based on the partial contribution of the following parameters: E_{redox} , pH, resistivity (ρ), RH and concentrations of Cl⁻ and SO₄²⁻. The characteristics of the various soil samples are given in Table 3.

As shown in Table 3 soils with resistivity of the order of 2–3 kΩ cm (S1–S5) present a partial contribution for the Steinrath index of (–2), while soils S6 to S8 with lower resistivities give a contribution of (–4). Concerning the pH, only the soil samples of pH 5 and 4 (S7 and S8) give a contribution of (–1) for the total Steinrath index.

Redox potential is one of the parameters that may have a strong influence on the total Steinrath index; soil samples with negative E_{redox} have a partial contribution of (–4) while those with $E_{\text{redox}} \geq 0$ give a null contribution.

Concerning the contribution of the chloride ions for the aggressivity, samples with chloride concentrations lower

Table 3 Physicochemical properties and degree of aggressivity of the soil samples named as S1 to S8

	S1	S2	S3	S4	S5	S6	S7	S8
$\rho/k\Omega\text{ cm}$	2.9 <i>-2</i>	3.5 <i>-2</i>	3.3 <i>-2</i>	2.6 <i>-2</i>	2.4 <i>-2</i>	0.13 <i>-4</i>	0.66 <i>-4</i>	0.32 <i>-4</i>
pH	7.9 <i>0</i>	7.9 <i>0</i>	7.9 <i>0</i>	7.9 <i>0</i>	7.9 <i>0</i>	7.9 <i>0</i>	5.0 <i>-1</i>	4.0 <i>-1</i>
$E_{\text{redox}}/V\text{vs. SCE}$	-0.28 <i>-4</i>	+0.12 <i>0</i>	-0.23 <i>-2</i>	-0.26 <i>-4</i>	-0.25 <i>-4</i>	-0.26 <i>-4</i>	0.00 <i>0</i>	-0.25 <i>-4</i>
$[\text{Cl}^-]/\text{mg kg}^{-1}$	17 <i>0</i>	17 <i>0</i>	25 <i>0</i>	55 <i>0</i>	150 <i>-1</i>	9,750 <i>-4</i>	17 <i>0</i>	17 <i>0</i>
$[\text{SO}_4^{2-}]/\text{mg kg}^{-1}$	190 <i>0</i>	190 <i>0</i>	190 <i>0</i>	190 <i>0</i>	190 <i>0</i>	190 <i>0</i>	190 <i>0</i>	190 <i>0</i>
RH/%	60 <i>-1</i>	100 <i>-1</i>	60 <i>-1</i>	60 <i>-1</i>	60 <i>-1</i>	60 <i>-1</i>	60 <i>-1</i>	60 <i>-1</i>
Total Steinrath index	-7	-3	-5	-7	-8	-13	-6	-10
Aggressivity	Low	Low	Low	Low	Medium	High	Low	Medium

Italicized values represent the partial Steinrath indexes

than 150 ppm present an almost null contribution for the total Steinrath index, while the concentration of 9,750 ppm rises it up to (-4).

Considering the Steinrath index, the soil sample S6 is highly aggressive, while sample S5 (150 ppm of Cl^-) and sample S8 (pH 4) are classified with medium aggressivity. All the others are classified as low aggressive. It should be noted that apart from sample S6, the other ones all present very low levels of chloride ions (17 to 150 ppm). Studies in soil should pursue for at least two or three chloride ion concentrations between 500 and 9,750 ppm.

Copper samples corrosion

Weight loss measurements

The average corrosion rates of the copper coupons exposed in the various soil samples, during a 3-month period, are given in Fig. 1. The differences between the weight losses of the two replicas were always lower than 2%. With the exception of the sample exposed to the soil with higher chloride concentration (Cu|S6), the corrosion rates varied between 4 and $12\ \mu\text{m year}^{-1}$, which means very good resistance against corrosion. The soil sample S2 is the one leading to the lowest corrosion rate, probably due to the lack of O_2 , particularly after a 3-month period, since this soil is water-saturated (RH=100%).

The corrosion rate obtained for the Cu|S6 interface falls in the range of the data published for Cu in seawater ($25\text{--}127\ \mu\text{m year}^{-1}$) [21].

Visual observations

Figure 2 presents a set of photos of one replica of the two copper coupons buried during 3 months in the soil samples. Figure 2a shows the effect of increasing the concentration of chlorides (17 to 9,750 ppm), while Fig. 2b shows the effect of pH, (7.9–4.0); Fig. 2c illustrates the influence of the relative humidity (60% and 100%), which turns to be

the effect of O_2 , since diffusion rates of O_2 through the air or through the liquids are drastically different. Figure 2d shows the effect of aeration.

The photos of Fig. 2 show copper samples, in general, with thin films of brown reddish colour covering the whole surface and other zones with corrosion of different extensions, depending on the aggressivity of the medium. The corrosion products formed on the attacked areas are brown reddish, grey to blue and green-coloured. The sample presenting higher amount of corrosion products (green) corresponds to the Cu|S6 interface.

As expected, the amount of corrosion products is much higher on the copper samples exposed to the soil sample S6 (the one with higher chloride concentration) and to the more acidic soil (S8). Areas with a grey to black colour could be seen on the coupon exposed to the water-saturated soil sample (S2, RH=100%).

Regarding the role played by the oxygen, the copper sample partially immersed in the soil (Cu_{2/3}|S1) presents the upper part (the one exposed to the air) with the appearance

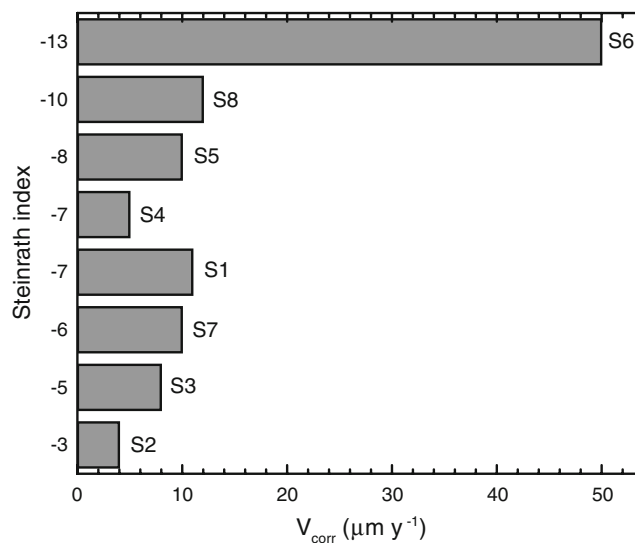


Fig. 1 Average corrosion rates vs. Steinrath index

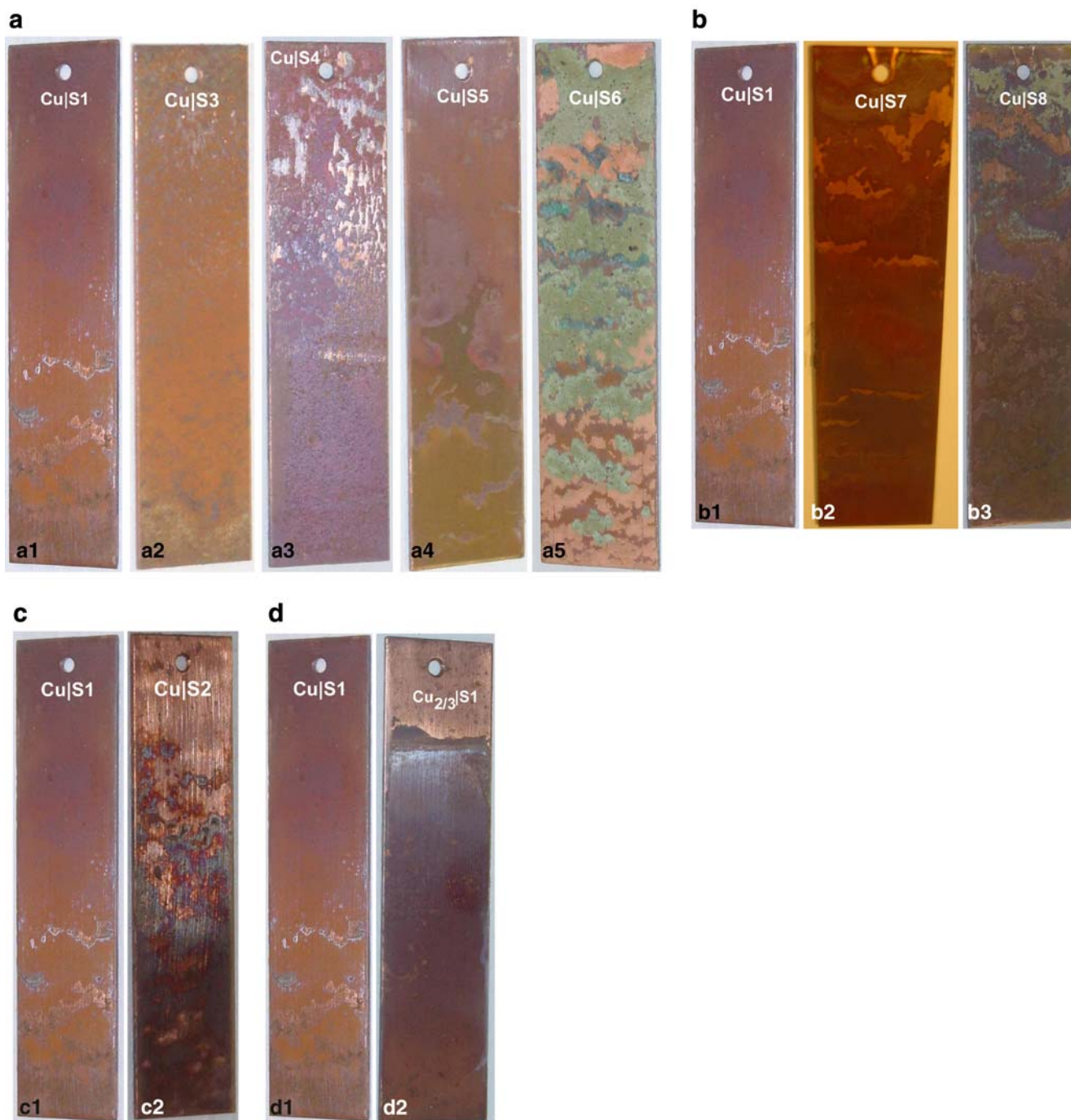


Fig. 2 Photos of the copper coupons with 3 months of exposure in the various soil samples: **a** effect of chloride concentration (17 to 9,750 ppm), pH 7.9, RH 60% (I–5); **b** effect of pH (7.9–4.0),

17 ppm Cl^- , RH 60% (I–3); **c** effect of relative humidity (60% and 100%) 17 ppm Cl^- , pH 7.9 (I–2); **d** effect of aeration (sample totally buried, 2/3 buried), pH 7.9, 17 ppm Cl^- and RH=60% (I–2)

of metallic copper (non-oxidised), while the portion of the sample in contact with the soil shows a quite uniform brown reddish film, covering the whole surface with higher intensity as going down. At the water–soil interface, the corrosion is slightly more heterogeneous, showing little amounts of white-bluish products. The formation of

aeration cells contributes to the localised corrosion process observed on the corresponding sample.

The visual observations are coherent with the gravimetric data. Actually, the soil samples S6 and S8 are the ones presenting higher Steinrath index and the respective copper samples are the ones showing higher attack. As shown by

the SEM images, the copper sample exposed to the soil sample S8 presents severe attack certainly due to pH effects.

SEM/EDS studies

Figures 3, 4 and 5 present SEM micrographs of the surfaces of the copper samples buried in the soil samples S2, S6 and S8, respectively.

The micrograph on Fig. 3a reveals uniform attack over the whole surface and grooves, probably related with the polishing process. With a higher amplification ($\times 3,000$) the attack is visible (Fig. 3b).

SEM micrographs of Fig. 4a, b show crystals with a hedgehog shape covering the entire zone analysed. In this zone, the corrosion products present a green colour and

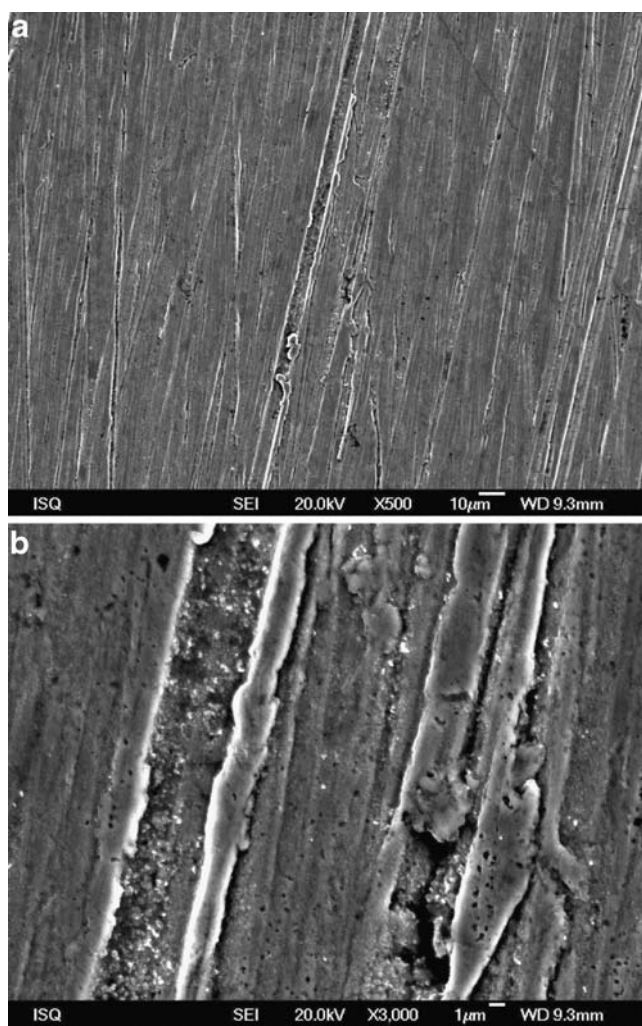


Fig. 3 SEM micrographs of the copper coupon exposed during 3 months to the soil sample S2 (17 ppm Cl^- , pH 7.9, RH 100%): **a** $\times 500$; **b** $\times 3,000$

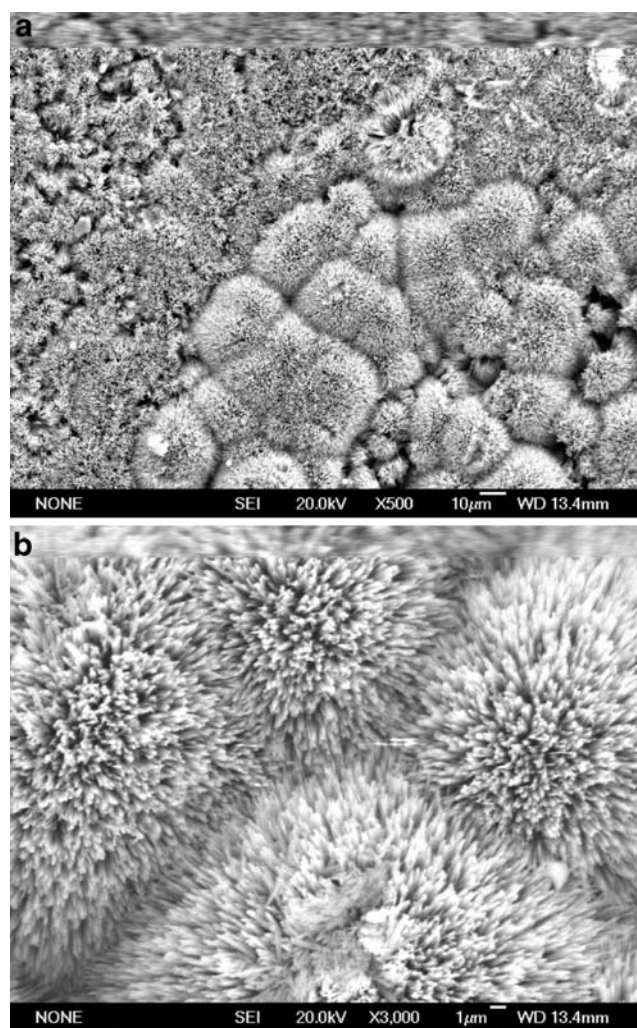


Fig. 4 SEM micrographs of the surface of the copper coupon exposed to the soil sample S6 (9,750 ppm Cl^- , pH 7.9, RH 60%): **a** $\times 500$; **b** $\times 3,000$

the corresponding EDS spectra show three main peaks attributed to Cu, O and Cl. Lower intensity peaks have been attributed to Na, K, Ca, Si, Fe and Al. These elements are certainly related with products from the soil composition. Most probably, the green corrosion products are basic copper chlorides on the top of a thin film of cuprite, Cu_2O . The film is quite dense. Figure 5a shows a surface almost uniformly attacked and microcrystallites covering the whole surface. After the removal of the corrosion products, one large pit can be seen in the micrograph of Fig. 5b.

The semi-quantitative analysis of EDS gives the approximate elemental composition of the corrosion products shown in Table 4. Data in Table 4 show that the polished copper surface presents apart from Cu (99%) only little percentages of Si (1%), presumably Si remaining from the

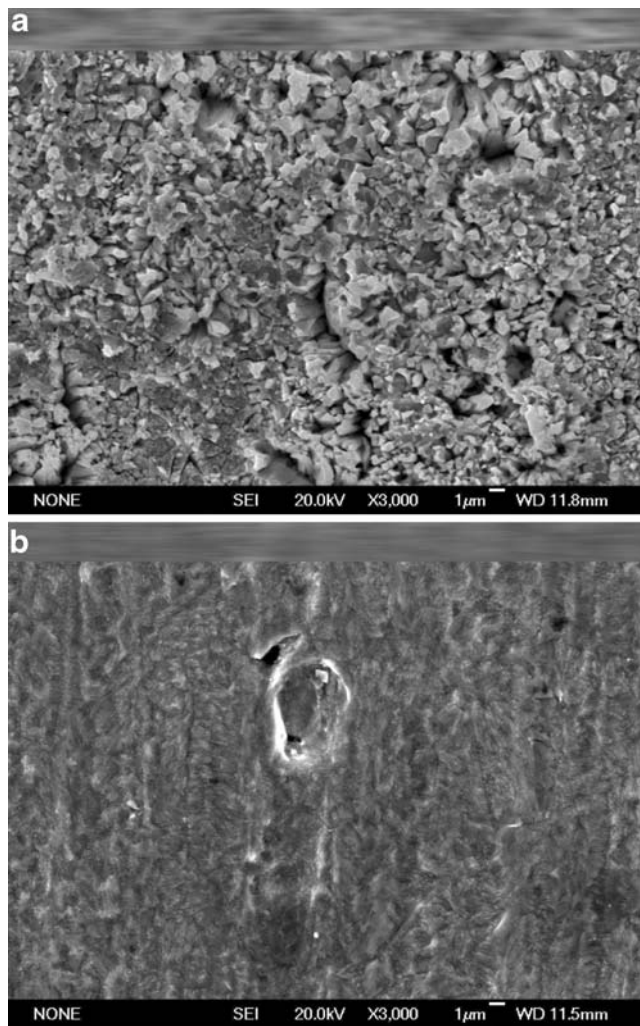


Fig. 5 SEM micrographs of the copper surface ($\times 3,000$) buried in the soil sample S8 (pH 4.0, 17 ppm Cl^- , RH 60%): **a** before the removal of the corrosion products; **b** after the removal of the corrosion products

polishing process. A sample buried 3 months in the soil sample S1 (pH 7.9, RH 60% and 17 ppm Cl^-) after being etched presents a composition identical to that of the blank sample.

Table 4 Semi-quantitative analysis from EDS data of the corrosion products on the copper surfaces

Copper coupons	Colours	Atomic percentage						
		O	Na	Al	Si	S	Cl	Cu
Unexposed	–	–	–	–	1	–	–	99
Etched after 3 months in S1	–	–	–	–	1	–	–	98
3 months in S2	Dark grey	–	4	–	1	1	–	93
3 months in S3	Brown reddish	28	2	1	1	–	1	67
3 months in S6	Dark green	67	–	–	10	–	6	17
3 months in S8	Light green	–	9	–	2	–	1	87
	Brown reddish	71	2	1	15	1	1	8

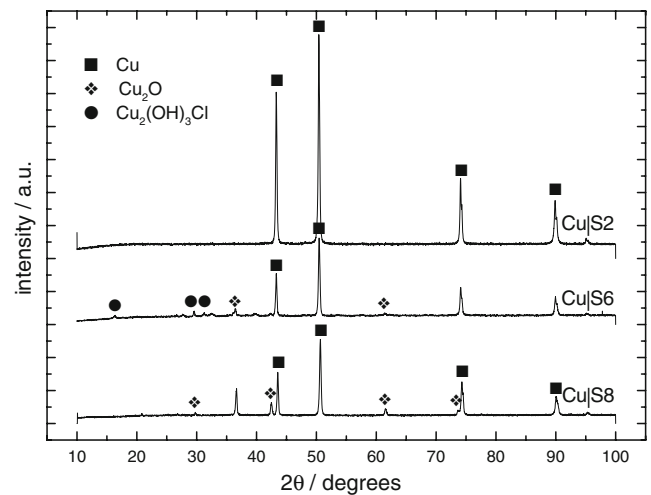


Fig. 6 XRD patterns of the corrosion products on the copper surfaces exposed during 3 months to the soil samples S2, S6 and S8

The corrosion products of brown reddish colour are mainly composed by O and Cu, while the light green products contain Cl and Cu and the dark green, O, Cl and Cu. The grey-coloured zones reveal a small percentage of S and no O, most probably copper sulphides. According to the literature [11, 12, 22, 23], for pure copper-containing minerals, the copper corrosion products formed under natural conditions, or artificially, often exhibit similar colours: red for Cu (I) oxide, green to blue for Cu (II) compounds, grey to black for the copper sulphides.

X-ray diffraction studies

Figure 6 gives the X-ray diffraction patterns of the corrosion products on the copper coupons exposed to the soil samples S2 (water-saturated), S6 (the one with higher amounts of chlorides) and S8 (the most acidic soil sample, pH 4). The identified crystalline corrosion products were cuprite, in the copper samples exposed to S6 and S8 soil samples, plus paratacamite on the copper sample exposed to the soil of high chloride concentration (S6). In spite of

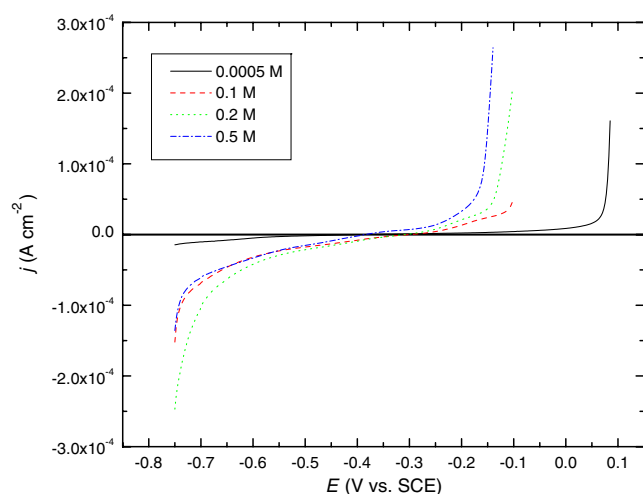


Fig. 7 Polarisation curves from copper electrodes immersed in solutions of pH 7.5 and chloride concentrations as given inside. $\nu = 1 \text{ mV s}^{-1}$

the differences that could be visualised already on the Cu|S2 interface, only the peaks due to Cu were observed on the corresponding XRD spectra, probably because the film is too thin and/or the products are not crystalline.

Electrochemical studies

Figure 7 presents a series of polarisation curves corresponding to copper polarised between -0.75 and $+0.10 \text{ V vs. SCE}$, at 1 mV s^{-1} , in deoxygenated solutions made with ‘soil washing water’ and different amounts of sodium chloride. To reduce the ohmic drop, NaClO_4 was added as the supporting electrolyte.

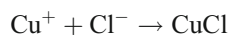
The application of the linear polarisation resistance method, LPR, to the sections of the curves of Fig. 7 in the narrow potential range of $\pm 20 \text{ mV}$ around $E(i=0)$ has produced the polarisation corrosion resistance (R_p) values given in Table 5. R_p values range between 4.3×10^4 and $0.8 \times 10^4 \Omega \text{ cm}^2$. Using the Stern–Geary equation with an average value of $B=0.020 \text{ V}$, the corresponding corrosion current densities have been calculated. On the other hand, the polarisation curves allowed the determination of the extension of the passive regions, ΔE_{pass} , which is reduced

as chloride concentration increases. Values of the passivity breakdown potential, E_b , are also given in Table 5, and a displacement to the negative direction is shown with increasing Cl^- concentration.

According to the literature [10] and references therein, the reaction rate-determining step in chloride media is suggested to be:



followed by the copper chloride formation:



Soluble Cu (I) chloride complexes can be formed as the chloride concentration increases.

The electrochemical data show a decrease in the polarisation resistance values and a consequent increase in the corrosion current densities, as the chloride concentration increases. Also, the passivity breakdown potentials are displaced to the negative direction, as expected.

In any case, it should be stated that the aqueous chloride solutions made with the washing water of soil sample S1 are a much less complex system than the soil sample. On the soil sample exposures, the buffering capacity of soils certainly contributes to reduce the corrosion rates, even when the cathodic reaction is the O_2 reduction, at least on the soil samples with $\text{RH}=60\%$. Concerning the absence of O_2 , the water-saturated soil sample S2 certainly contains very low oxygen levels, comparable to the deoxygenated neutral aqueous solutions used for the electrochemical studies.

However, it should be emphasised that electrochemical techniques are useful tools to evaluate instantaneous corrosion rates and breakdown potentials, while the weight loss technique evaluates average corrosion rates over different exposure times.

Conclusions

This study identifies the influence of certain soil properties on the corrosion of copper. The effects of chloride concentration, oxygen availability and soil acidity were investigated.

Table 5 Electrochemical data from the analysis of the polarisation curves

[Cl ⁻] (mol dm ⁻³)	E_b (V vs. SCE)	ΔE_{pass} (V vs. SCE)	LPR analysis	
			R_p ($\Omega \text{ cm}^2$)	j_{corr} ($\mu\text{A cm}^{-2}$)
0.0005 (17 ppm)	+0.040	0.42	4.3×10^4	0.5
0.1	-0.12	0.23	1.6×10^4	1.2
0.2	-0.14	0.21	1.0×10^4	2.0
0.5	-0.17	0.18	0.8×10^4	2.6

The level of corrosion rates (low, average or high) expected from the degree of aggressivity of the various soil samples, classified according to the Steinrath index, is in reasonable agreement with the data obtained from the 3-month exposures in the various soil samples. The more aggressive soil sample (S6) with the Steinrath index of (−13) leads to an average corrosion rate of $50 \mu\text{m year}^{-1}$, while the soil sample with the lowest Steinrath index (−3) originates the lowest corrosion rate ($4 \mu\text{m year}^{-1}$). All the other results present good coherence.

The influence of the humidity degree with the consequent reduction of O_2 levels can be visualised on the copper samples exposed to the water-saturated soil sample (S2, RH=100%), which show the lowest value of average corrosion rate. The effect of the aeration cells formation is also well visible on the copper samples half buried in the soil sample S1. Photographs of the copper sample immersed in the soil sample S2 show grey-coloured zones, presumably copper sulphide, since the EDS spectra have revealed the presence of S. Most likely, the anaerobic conditions in the soil sample particularly on the bottom of the beaker may be responsible for the formation of copper sulphide, due to the activity of the anaerobic sulphate reducing bacteria.

The EDS data allowed advancing the identification of the green-coloured corrosion products, as being basically basic copper chlorides, such as paratacamite and/or atacamite and cuprous oxide, Cu_2O , the compound giving the brown reddish film observed in all the samples.

X-ray diffraction analysis has identified cuprite in the copper samples corresponding to the interfaces Cu|S6 and Cu|S8, plus paratacamite on the copper coupon exposed to the soil with higher concentration of chloride (S6). In spite of the visual differences noticed on the copper coupon buried in the S2 soil sample, the XRD spectra present only peaks attributed to Cu. Most probably, the films formed are too thin and non-crystalline.

Electrochemical studies performed with copper electrodes immersed in deoxygenated neutral aqueous solutions, containing the soil soluble species and different concentrations of chloride ions, allowed the determination of the polarisation resistances and the corresponding corrosion current densities. The obtained values show to vary with chloride concentration, as expected.

Finally, our study has proved that the soil characteristics (degree of aggressivity) are able to predict the corrosion resistance behaviour of copper samples buried in soils of different degrees of aggressivity.

Also, the breakdown potentials calculated from the electrochemical polarisation curves present good coherence with the chloride levels. They may constitute a valuable tool to predict pitting corrosion susceptibility of buried metallic copper samples in soils contaminated

with chloride ions, with no sample removal from soil matrices. Studies of copper corrosion should pursue with soils samples modified with chloride concentrations between 500 and 9,750 ppm.

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