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Investigation on copper corrosion behaviour in industrial waters by electrochemical noise analysis

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This paper represents an attempt to apply electrochemical noise analysis to monitor copper corrosion rates in solutions simulating near neutral or acidic industrial waters, containing chloride, sulphate and bicarbonate ions. The very low noise levels characterizing these systems make the evaluation of the noise resistance possible only with a four electrode arrangement, where the electrode couples used to detect the voltage and current fluctuations have different surface areas. This arrangement is probably a handicap to the evaluation of the polarization resistance values from noise resistance data. Cyclic voltammetries were carried out in order to investigate the nature of the corrosion products obtained in solutions with different pH.

Keywords: *copper*, *corrosion*, *electrochemical noise*, *industrial waters*, *cyclic voltammetry*

1. Introduction

Many studies concern the applicability of electrochemical noise analysis as a nonperturbative technique suitable, in some cases, to quantitatively evaluate corrosion rates [1–4]. However, few studies deal with the use of this technique to investigate copper corrosion behaviour. Bertocci [5] derived impedance plots from the voltage and current noise spectra recorded on copper electrodes immersed in a copper sulphate/sulphuric acid solution. Smith and Francis [6] found that the electrochemical current noise could characterize carbon film-bearing copper tubes with respect to their ability to support pitting corrosion. Their method was adopted by Sandenbergh *et al.* [7] with results partially in contrast with those obtained by the former authors. Organic substances added as inhibitors of crevice corrosion of copper in sodium chloride solution were efficiently screened by the analysis of the electrochemical current noise [8]. Loto *et al.* [9] analysed the fluctuations of the corrosion potential of stressed alpha-brass specimens exposed to a Mattsson solution at pH 7.2. They observed that the clearest indication of specimen cracking was the measurement of high noise power values.

This paper describes an attempt to apply electrochemical noise analysis to evaluate the corrosion rate of copper electrodes exposed to aqueous solutions whose chloride and sulphate ion contents are about tenfold those of a common tap water and whose pH values, ranging from 5.5 to 8.4, are determined by the equilibrium between carbon dioxide and bicarbonates. A solution at pH 3.0, obtained by hydrochloric acid addition, with the same chloride and sulphate ion contents as the previous ones, was also used in this investigation. These solutions simulate the aggressivity of near neutral or acidic industrial waters.

2. Experimental details

Different types of electrodes were prepared from DHP (deoxidized high phosphorus) copper bars:

(i) copper sheets (area 7300 mm^2) electrically connected to the wires by spot welding, with the connection masked off with epoxy;
(ii) cylinders (area 1020 mm^2) where the electrical connection was ensured by a threaded rod screwed into the electrode itself and was screened from the aggressive solutions by a glass tube and Teflon gaskets; and
(iii) copper discs (area 20 or 3.1 mm^2) obtained by embedding cylinders with reduced diameter in epoxy resin and exposing the transversal section to the aggressive solutions.

All the specimens were ground with n. 600 emery paper and degreased with acetone.

The aggressive solution was obtained by suspending 0.3 $g\,dm^{-3}$ calcium carbonate in a solution containing 1.13 $g\,dm^{-3}$ sodium sulphate and 0.50 $g\,dm^{-3}$ sodium chloride. Carbon dioxide was then bubbled to dissolve calcium carbonate. By air bubbling, the solution was adjusted either to pH 7.0 ± 0.25 or pH 8.4 ± 0.1. Without air bubbling, the solution pH was 5.5 ± 0.25. Solutions with pH values of 3.0 ± 0.25 were obtained by adding 10^{-3} M HCl to a solution containing 0.44 g dm^{-3} calcium chloride dihydrate and 1.13 g dm^{-3} sodium sulphate. 0.058 g dm^{-3} sodium chloride was also added to keep the sulphate, chloride and calcium ion contents equal to those of the other solutions.

Linear polarization resistance measurements were carried out during three days of immersion in the solutions at the four pH values investigated (voltage range: ± 8 mV vs E_{corr}; scan rate: 0.1 mV s^{-1}).

The arrangement to detect current noise fluctuations consisted of two 'identical' electrodes connected to a home-made zero resistance ammeter (ZRA). Groups of 8192 current readings, collected at 0.1 s interval, were acquired by a high resolution multimeter and sent to a computer through an IEEE 488 NI interface. From each group of 8192 readings, four partially overlapped groups of 4096 readings were extracted to compute, after linear trend removal, four power spectrum density plots, by a fast Fourier transform algorithm. After averaging, only one PSD plot with reduced scatter was obtained, covering the frequency range from 0.002 to 5 Hz. Noise power values, in the range 0.002–1 Hz, were also calculated and plotted against immersion time for up to 48 h of immersion.

The voltage fluctuations were detected from another couple of two 'identical' electrodes, so that the voltage and current fluctuations were completely uncorrelated. The frequency range investigated was the same as for the current data.

To investigate the nature of the surface film formed on copper under the different conditions, cyclic voltammetry was carried out on electrodes of type (iii) with surface area 20 mm^2. The cycles were usually between 0 and −0.9 V with respect to the saturated calomel electrode (SCE) and the scan rate was 10 mV s^{-1}. The high vertex potential was close to the corrosion potential of the electrodes under the adopted experimental conditions, while the low vertex potential was cathodic enough to reduce all the products in the surface film.

All the potentials quoted in the paper are referred to the SCE.

3. Results and discussion

3.1. *Linear polarization resistance measurements*

Figure 1 shows the $1/R_p$ values during immersion in solutions at different pH, while Fig. 2 gives the trends of the corresponding corrosion potentials. Under the adopted experimental conditions copper suffers uniform corrosion attack. $1/R_p$ values give an indication of copper corrosion rates and gradually increase at decreasing pH values.

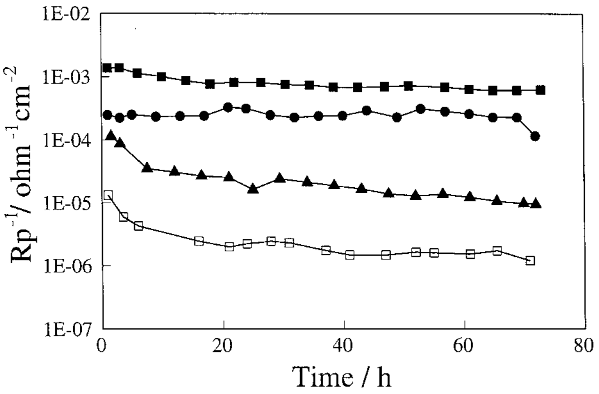

Fig. 1. Reciprocals of the polarization resistance values obtained on copper electrodes in solutions at pH 3.0 (■); 5.5 (●); 7.0 (▲) or 8.4 (□).

3.2. *Cyclic voltammetries*

Cyclic voltammetries were carried out under aerated conditions to identify the corrosion products obtained from copper electrodes exposed to the different aggressive solutions. Comparative tests were carried out under deaerated conditions in the case of solutions at pH 3 and 8.4, as these pH values were not affected by deaeration. Some voltammograms at pH 5.5 under deaerated conditions were obtained in an acetate buffer containing the same chloride and sulphate ion contents of the original pH 5.5 solution.

At pH 3.0 the voltammogram of Fig. 3 is obtained. Copper oxidation begins at about −0.1 V and copper reduction appears to occur immediately at the scan reversal. A further large reduction peak is visible at about −0.45 V, which was attributed to oxygen reduction, as it appears even if the potential is scanned between −0.2 and −0.9 V, where copper oxidation is not possible. Even under deaerated conditions, copper oxidation begins at about −0.1 V, while no reduction peak is visible until about −0.7 V, where reduction of hydrogen ions occurs. It was concluded that copper is oxidized to soluble species under deaerated conditions, which quickly diffuse away from the electrode and are little reduced. Under these conditions, a bare metallic surface is expected which

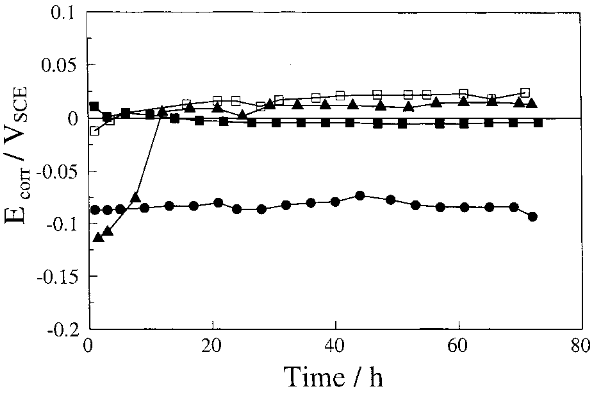

Fig. 2. Corrosion potentials measured on copper electrodes exposed to solutions at different pH values. Symbols as in Fig. 1.

appears to exhibit a low overvoltage for hydrogen evolution. Therefore, the reduction peak observed in Fig. 3 was attributed to the reduction of an insoluble species, probably CuCl. The Figure also shows that the charge involved in the reduction peak (220 μC) is smaller than that obtained from the integral of the oxidation peak (310 μC). This difference would be even more pronounced if the oxygen reduction current could be subtracted from all the current values and suggests that copper oxidation mainly produces soluble species, probably $CuCl_2^-$, whose formation is not hindered by the insoluble product.

These tests also stress the importance of carrying out the tests under the same conditions of aeration as those of interest, as different oxidized copper species are formed.

At pH 5.5, the voltammograms obtained are similar to those obtained at pH 3, with a further reduction shoulder around −0.15 V (Fig. 4). Also in this case a large peak around −0.45 also remains unchanged in the absence of any copper oxidation (voltage range −0.1 to 0.9 V) and may be ascribed to oxygen reduction. Again, the voltammograms obtained under deaerated conditions show a marked copper oxidation without any reduction peak, beside hydrogen ion reduction. This suggests that the reduction peak at −0.05 V, obtained without nitrogen bubbling, must be associated with an insoluble species and the integral of the current with time suggests the concomitant formation of soluble copper oxidation products. If, at each voltage reversal, the electrode is kept at 0 V for 60 s the shoulder becomes a more pronounced peak, centred around −0.27 V, (Fig. 5) which, in agreement with literature data obtained at pH 5 [10], can be attributed to Cu_2O reduction and is thermodynamically stable over −0.1 V, at pH 5.5. According to the Pourbaix diagram for the five-component system $Cu–Cl–CO_2–SO_3–H_2O$, with component concentrations close to those adopted here [11], the condition of 0 V and pH 5.5 is at the borderline between different oxidized copper species, that is Cu^{2+}, Cu_2O and $CuCO_3.Cu(OH)_2$. Therefore, the first reduction peak could be related to the last insoluble product. However, if the high vertex potential is decreased to −0.075 V, with a dwell of 60 s at this potential at each cycle, only a limited amount of copper oxidation and reduction occurs. This vertex potential corresponds to the corrosion potential of copper electrodes at this pH and is only slightly nobler than the equilibrium potential for the couple Cu/Cu_2O.

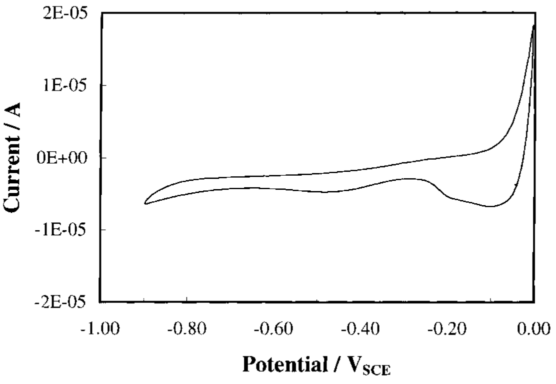

Fig. 4. Cyclic voltammetry obtained on copper electrodes exposed to the aggressive solution at pH 5.5 (5th cycle).

Figure 6 shows the voltammetries obtained in the solution at pH 7.0, by cycling between 0 and −0.9 V and dwelling for 60 s at 0 V (2nd and 3rd cycles).

The anodic peak obtained at about −0.05 V corresponds to copper oxidation to Cu_2O [11], which is followed by the beginning of another anodic peak which corresponds to the further oxidation of this copper oxide. To investigate the nature of the species reduced at about −0.55 and −0.73 V, voltammetry in the range from −0.1 to −0.9 V, with 60 s dwell at −0.1 V was carried out. In this case, only Cu_2O is formed and the reduction peak at −0.45 V (Fig. 7) corresponds to its reduction to copper. According to the Pourbaix diagram, the copper product obtained by further oxidation of this oxide is $CuCO_3.Cu(OH)_2$ (malachite) whose reduction to Cu_2O and Cu, according to the following reactions:

$$CuCO_3.Cu(OH)_2 + H^+ + 2e^- \rightarrow Cu_2O + HCO_3^- + H_2O$$

$$Cu_2O + 2H^+ + 2e^- \rightarrow 2Cu + H_2O$$

is probably responsible for peaks 1 and 2 in Fig. 6. It is puzzling that peak 2 becomes higher than

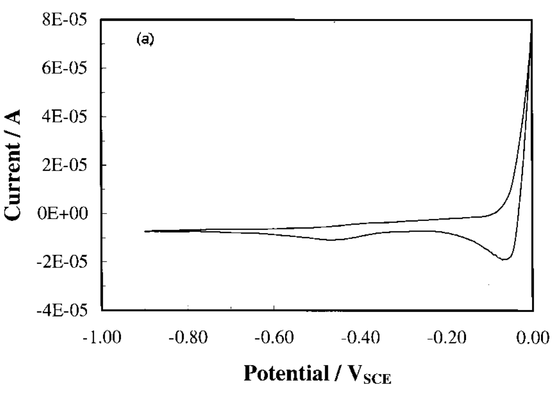

Fig. 3. Cyclic voltammetry obtained on copper electrodes exposed to the aggressive solution at pH 3.0 (5th cycle).

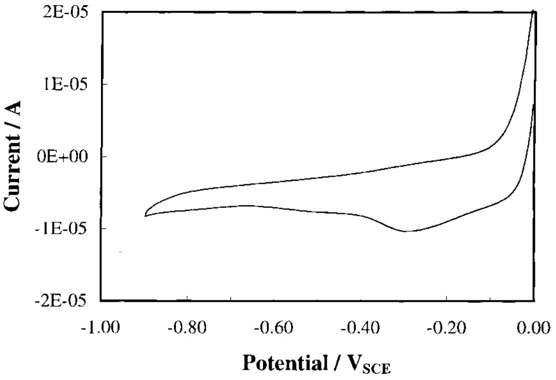

Fig. 5. Cyclic voltammetry obtained on copper electrodes exposed to the aggressive solution at pH 5.5 with 60 s waiting at 0 V (5th cycle).

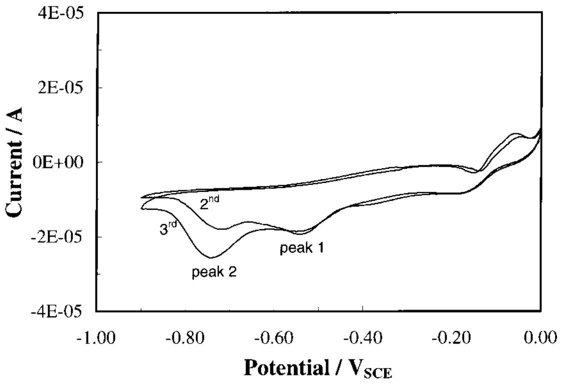

Fig. 6. Cyclic voltammetry obtained on copper electrodes exposed to the aggressive solution at pH 7.0 (2nd and 3rd cycles).

peak 1. This can occur if oxidation of Cu_2O to $CuCO_3.Cu(OH)_2$ is incomplete, with a resulting duplex surface film whose outer layer, consisting of basic copper carbonate, is compact and insulating enough to prevent the inner layer from reduction, until the outer layer is reduced, at sufficiently cathodic potentials. Therefore, the malachite film is reduced at more active potentials than the film constituted of only cuprous oxide (Figure 7), suggesting it is a protective kinetically-stable film.

At pH 8.4, no marked difference in the voltammetry appears, suggesting the formation of the same oxidation products on the copper electrodes and, as at pH 7.0, no evidence is found for the formation of soluble oxidized copper species.

Some considerations concerning copper under free corrosion conditions can be inferred from these tests. At pH 3.0, copper is dissolved to some soluble products. An insoluble nonprotective corrosion product is also detected, probably CuCl. At pH 7 and 8.4 copper is passive, owing to the formation of an insulating film, probably a duplex film of basic copper carbonate over copper (I) oxide, in agreement with the results obtained by other authors which present an extensive analysis of copper corrosion in the presence of oxygen, carbon dioxide and different dilute salt solutions [12–15]. At the corrosion potential obtained at pH 5.5, copper is covered by a Cu_2O layer, whose protectivity, according to linear polarization resistance values, is intermediate between that afforded by the films formed at pH 3.0 and 7.0. This film is reported to be porous and not very protective, as the primary adherent film is broken up by mechanical strain at an early stage on increasing thickness [12–15] and the corrosion process is often controlled by diffusion of soluble copper species through it [16].

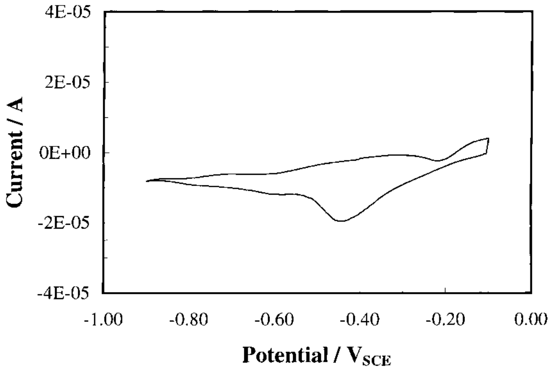

Fig. 7. Cyclic voltammetry obtained on copper electrodes exposed to the aggressive solution at pH 7.0 with 60 s waiting at −0.1 V (5th cycle).

3.3. *Noise measurements*

From the analysis of the voltage and current fluctuations, recorded at different immersion times, it is possible to calculate a parameter, R_n, defined as

$$R_n = (\sigma_V/\sigma_I)(A_V A_I)^{0.5} \tag{1}$$

where σ_V and σ_I are the standard deviations of the voltage and current fluctuations, respectively, evaluated at the same exposure period, while A_V and A_I are the total areas of the electrodes used to monitor, respectively, the voltage and current noise [17]. In the present work the standard deviations were substituted by the square roots of the voltage and current noise power values (denoted $\langle V^2 \rangle$ and $\langle I^2 \rangle$, respectively), obtained from the integration of the PSD (power spectrum density) plots, on the basis of the following equivalence [18–20]:

$$\sigma_x = \int_0^{+\infty} \Psi_x(f)\,df \tag{2}$$

where $\Psi_x(f)$ is the PSD of the fluctuations in the x variable (in this case current or voltage). The integration was restricted to the range 0.002 to 1 Hz, that is the range where the electrochemical noise was found higher than the instrumental noise, under the experimental conditions thereafter described. With the adopted experimental arrangement, A_V and A_I correspond to the double of the area of each electrode.

R_n was often found to be a good estimation of the polarization resistance, R_p [21, 22], and an attempt was made to check it by comparing the R_n values to the R_p values of Fig. 1.

At first, electrodes with area of 1020 mm^2 were used to monitor both the voltage and current noise. However, the voltage noise power values were extremely scattered and often close to the detection limit of the technique. No clear difference among the trends obtained at different solution pH values was evident. The current noise power values were close to the detection limit of the technique at pH 7 and at pH 8.4. The theoretical models proposed to explain the equivalence between R_n and R_p deduce a direct proportionality between the noise power and the electrode area, in the case of the current noise power [17] and an inverse proportionality, in the case of the voltage noise power [17, 23]. Therefore, bigger electrodes with area of 7300 mm^2 each were used for current noise measurements at pH 7.0 and 8.4, while smaller electrodes, with area 3.1 mm^2 were used for voltage noise measurements.

The $\langle I^2 \rangle$ values obtained at pH 3 and 5.5 on electrodes of 1020 mm^2 area are reported in Fig. 8, together with the $\langle I^2 \rangle$ values obtained at pH 7 and 8.4 on electrodes of 7300 mm^2. All of them were normalized for the different areas.

Figure 8 shows that increasing $\langle I^2 \rangle$ values are obtained at lower solution pH values, that is under more aggressive conditions, as suggested by the $1/R_p$ trends exhibited in Fig. 1. This is in agreement with the equivalence between R_n and R_p.

The voltage noise power values obtained on small electrodes are collected in Fig. 9(a) and (b). The scattering of the voltage noise power values is much higher than that of the current data (Fig. 8), particularly at pH 5.5. Therefore, while Fig. 8 gives qualitative information concerning the corrosion currents, Fig. 9 does not afford any clear indication.

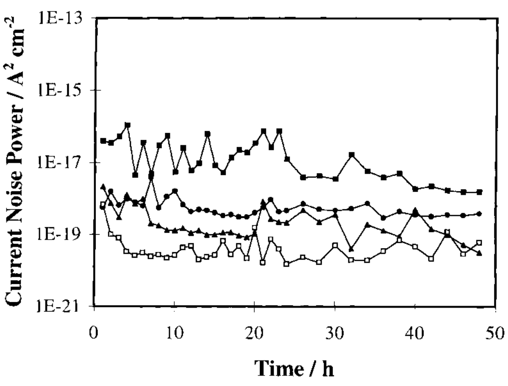

Fig. 8. Current noise power values measured on copper electrodes exposed to solutions at different pH values. Symbols as in Fig. 1.

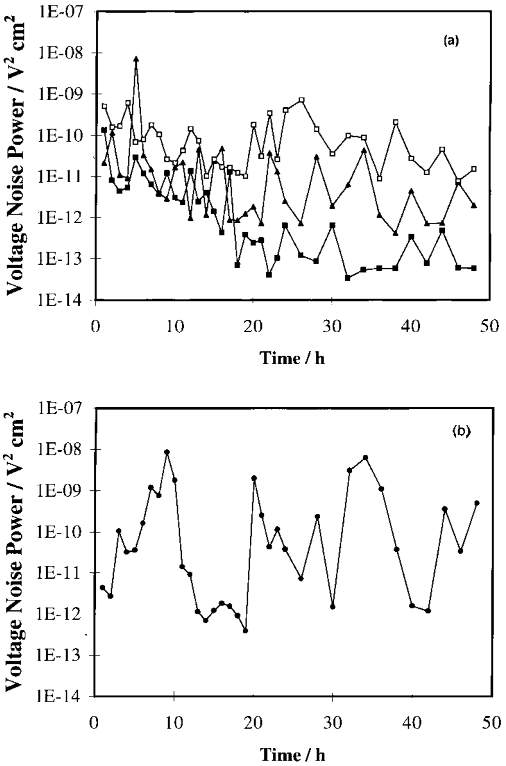

Fig. 9. Voltage noise power values measured on copper electrodes exposed to solutions at pH 3.0, 7.0 and 8.4 (a) and at pH 5.5 (b). Symbols as in Fig. 1.

Figure 10(a) and (b) collect the $1/R_n$ values calculated from the data of Figs 8 and 9. The comparison between Figures 1 and 10 shows only a qualitative agreement, as the R_n values are more or less one order of magnitude lower than the R_p values. Moreover, the scatter of the R_n values, due to the scatter of $\langle V^2 \rangle$, makes this comparison difficult.

The cause of the differences between the data shown in Figs 1 and 10 are discussed on the basis of a model recently elaborated [3, 4].

According to this model, with a measurement scheme consisting of two noisy and one noiseless reference electrode arrangement, it is found that:

$$R_{sn}(f) = |Z(f)|$$

($R_{sn}(f)$ is the spectral noise impedance, defined as $R_{sn}(f) = (\Psi_V(f)/\Psi_I(f))^{0.5}$, and $|Z(f)|$ is the impedance of each electrode) if the following conditions are satisfied: (i) the identical electrodes have the same impedance and (ii) the solution resistance between them is much lower than the electrode impedance. Moreover, under these circumstances, $R_n = R_p$ if (iii) these electrodes are also identically noisy and (iv) R_{sn} is constant and equal to R_p, in the frequency bandwidth investigated. No restriction on the type of corrosion attack, either uniform or localized, is necessary for the validity of these findings.

In the case of a four identical electrode arrangement,

$$R_{sn}(f) = 2|Z(f)|$$

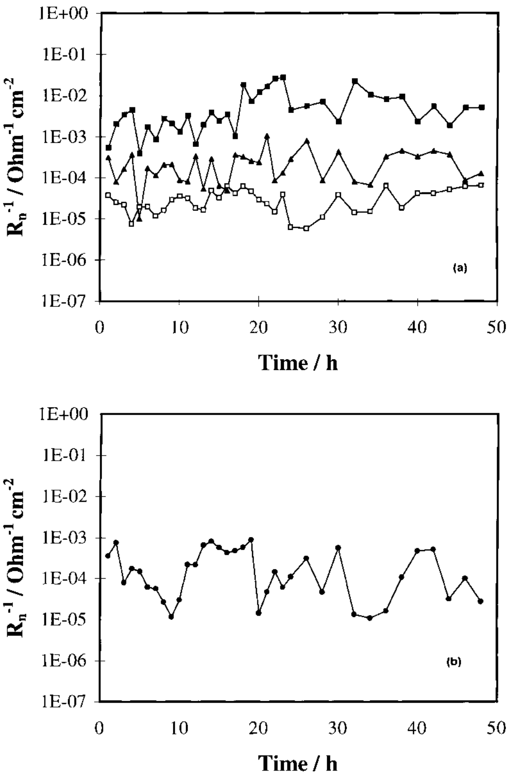

Fig. 10. Reciprocals of the noise resistance values obtained on copper electrodes exposed to solutions at pH 3.0, 7.0 and 8.4 (a) and at pH 5.5 (b). Symbols as in Fig. 1.

if the conditions (i), (ii) and (iii) are satisfied. Also, in this case R_n gives information about R_p, being $R_n = 2R_p$, if condition (iv) is also satisfied.

With this type of arrangement the possibility of quantitatively evaluating R_p is difficult because, as the authors [3, 4] pointed out, it is rarely verified that the electrodes used to detect voltage fluctuations, connected to a high impedance measuring device, have the same noise level of the electrodes connected to a ZRA and crossed by the short circuit current. The low noise level detected on copper in the environments investigated here made the evaluation of voltage and current fluctuations critical, so that it was necessary to use electrode couples of different areas to appreciate both the current and the voltage noise. The four electrode arrangement and the use of a normalization technique were therefore a compulsory choice to the evaluation of R_n values.

The calculation of the $R_{sn}(f)$ spectra at different pH values and at different immersion times showed that condition (iv) is satisfied at pH 3, where flat $R_{sn}(f)$ spectra are obtained in the frequency bandwidth investigated. At pH 7.0 and 8.4 the $R_{sn}(f)$ spectra have a low frequency limit with constant $R_{sn}(f)$ values over more or less one frequency decade. In contrast, at pH 5.5 the $R_{sn}(f)$ values always increase at decreasing frequencies, thus preventing the estimation of the zero frequency limit of the impedance, by either d.c. or a.c. methods under the experimental conditions here adopted. As an example, Fig. 11 reports the spectra obtained at 10 h of immersion in solutions at pH 3.0, 5.5 and 8.4.

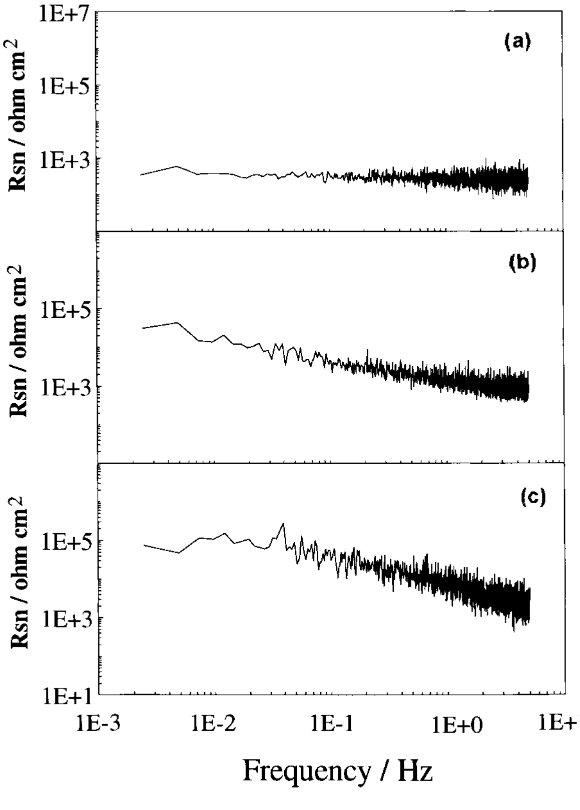

Fig. 11. R_{sn} spectra obtained after 10 h of immersion in solutions at pH 3.0 (a), 5.5 (b) and 8.4 (c).

With the exception of pH 5.5, the $1/R_n$ values were recalculated from noise power values obtained from the integration in the lowest frequency decade, 0.002–0.02 Hz, where the $R_{sn}(f)$ spectra are flat, even at pH 7 and 8.4. No marked difference with respect to Fig. 10(a) is obtained, as only a limited decrease of the $1/R_n$ values was found at both pH 7.0 and 8.4 and no marked difference at pH 3.0.

Condition (ii) is satisfied as the electrodes were close to each other, so that the solution resistance between them was about one tenth of the electrode impedance, at pH 3 and relatively smaller at higher pH values.

These data suggest that at pH 3.0, 7.0 and 8.4 the noise analysis gives only a qualitative estimate of the polarization resistance values, probably owing to the difficulty in satisfying condition (iii). At pH 5.5, the low frequency limit of the impedance is not achieved and the reason possibly being diffusion control of the corrosion process, as is frequently found on copper protected by a cuprite film.

4. Conclusions

The tests carried out to investigate copper corrosion behaviour in solutions simulating near neutral or acidic industrial waters show the following:

(i) The arrangement for electrochemical noise analysis consisting in two noisy and one noiseless electrode arrangement cannot be adopted, owing to the low noise levels characterizing this system.
(ii) At pH 3.0, 7.0 and 8.4, the R_n values obtained from electrochemical noise analysis give only a qualitative estimate of the polarization resistance values, probably owing to the difficulty of having four equally noisy electrodes.
(iii) As quantitative analysis is beyond the capability of the technique, the comparison of the current noise power values appears to be the simplest way of obtaining qualitative information for copper corrosion rates.
(iv) The high aggressivity towards copper obtained at pH 3 is due to the formation of a nonprotective insoluble film, probably constituted by CuCl, which does not hinder the simultaneous dissolution of the metal to soluble species.
(v) At pH 5.5 copper appears to be covered by a porous cuprous oxide layer which does not completely hinder the direct oxidation of copper to soluble products.
(vi) At pH 7 and 8.4 copper is passive: the protective surface film is probably duplex in nature and consists of a cuprous oxide layer topped by a highly-resistive basic cupric carbonate layer.

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