Corrosion and scale studies of copper used in Moroccan industrial cooling water systems

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Abstract The corrosion and scale behavior of copper in industrial cooling water system were investigated via electrochemical measurements, ionic chromatography, SEM/EDAX, and X-ray diffraction analyses. It was found that the studied water has a corrosion and scale character. The EDAX and XRD analyses indicated that the major corrosion and scale products were the CuO_2 and CaCO_3 , respectively. In addition, the middle Mueller–Hinton test was also employed to evaluate the development of microorganisms for copper in make-up water solution. It is noted that bacterial colonies appeared after immersion of samples in make-up water, indicating that this water develops bacterial colonization. Finally, the influence of some operating parameters on the corrosion and scale rate was studied. It was shown that the scale rate increases with pH, temperature, and the addition of chloride and sulfide ions. It was also found that the corrosion rate increases with temperature and chloride ions and decreases with pH and immersion time.

Keywords Corrosion · Scaling and microorganism · Copper · Industrial cooling water · SEM/EDAX · XRD · Ionic chromatography

Introduction

Owing to their excellent proprieties, copper and its alloys are used in several important industries (Elbakri et al. 2008). However, they are susceptible to different forms of corrosion such as pitting corrosion. So, the water used as a thermal fluid in cooling circuits usually leads to three problems, namely, corrosion, scaling, and microorganism development. These phenomena are the source of a loss of the metallic material, a decrease of the thermal efficiency of the circuit, and the proliferation of microorganisms in the water, respectively, (Tourir et al. 2010; Srisuwan et al. 2008). Indeed, iron is the principal redox-active metal in the metabolic processes of essentially all living organisms. It is either involved in catalytic quantities as a component of a large number of proteins, or at much higher substrate amounts as the external electron donor or acceptor for specially adapted environmental microorganisms called ‘iron bacteria’ (ferrotrophic bacteria, aerobic or anaerobic) or ‘iron bacteria’ respectively (Enning et al. 2012). In most biological functions, iron has the state of oxidation +II (ferrous) or +III (ferric). From a physiological point of view, it appears astounding that also the native, metallic element (Fe^0) can be involved in a biological process; this is anaerobic microbial corrosion. In technology, the process is often referred to as microbially influenced corrosion (MIC) (Enning et al. 2012; Hamilton 1985; Lee et al. 1995).

However, the bio-corrosion is the effect of microorganisms on the kinetics of the corrosion processes of materials; whereas the bio-film is the adherence of these microorganisms on the corroded wall (Chantereau 1980). So, the microorganisms are bacteria belonging to the family of Gram-aerobic or facultative anaerobic Enterobacteriaceae, namely *Escherichia coli*, *Klebsiella*

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pneumoniae pseudomonadaceae, *Pseudomonas aeruginosa* and Achromobacteriaceae (*Bacillus subtilis*). Therefore, the bio-film has evolved over time depending on the bacteria that make it up. So, the bio-film is composed not only of water and bacteria but also of organic substances secreted by microorganisms or lysis of bacteria. These are extracellular exopolymers.

Usually, the use of acid in order to remove scale caused a risk for materials (corrosion). However, the scale deposition can, in some cases, protect the pipes against corrosion. Indeed, the presence of a certain quantity of CO₂ is necessary for it is neither aggressive nor calcifying. If this amount was large, the water was aggressive and was therefore not calcifying. For this, many calculation methods have been proposed to determine the scaling tendency.

On the other hand, the corrosion phenomenon is a serious global problem for metallic materials (Qiang et al. 2016; Herrmann et al. 2014). As a very classic example, copper is the most important metal used in industries, which can be corroded seriously in the marine environment due to the existence of aggressive chloride ions (Chen et al. 2012; Sherif and Park 2005).

However, Kartsonakis et al. studied the copper corrosion inhibition in industrial cooling water systems by electrochemical techniques and microscopic observations. They found, under specific conditions (e.g., high pH), that the studied water has a corrosive character (Kartsonakis et al. 2015).

On the other side, to attenuate or eliminate these problems, waters used in cooling circuits are treated with inhibitive formulations. So, Tourir et al. studied the influence of sodium gluconate (SG) associated with cetyltrimethylammonium bromide (CTAB) on low-carbon steel corrosion in simulated cooling water using electrochemical measurements. They showed that the obtained formulation has good inhibition for low-carbon steel corrosion in the studied medium (Tourir et al. 2014).

In addition, Soror studied the effect of polyacrylamide on carbon steel and copper corrosion in simulated cooling water using scale, Tafel, linear polarization measurements, and optical microscopy. He obtained that the this polymer decreases scale build-up growth and acts as an anodic-type corrosion inhibitor of carbon steel and mixed-type of copper (Soror 2009).

Therefore, the objective of the present work is to study the corrosion and scale of copper in a cooling water system using electrochemical measurements, ionic chromatography, SEM/EDAX, and XRD analyses. The middle Mueller–Hinton test was also employed to assess the microorganisms development. Indeed, the effect of some operating parameters on the corrosion and scale process of copper was investigated.

Experimental procedure

Presentation of the water study conditions

In this study, we have taken as a corrosive medium a solution of water used in cooling circuits of the foundry of the MAC/Z Company of Skhirat/Morocco. In order to ensure a satisfactory conservation of the physicochemical characteristics of the used water, samples of representative homogeneous water were taken in clogged, protected, isothermal containers in the dark at temperature of 277 ± 2 K. In addition, in order to avoid any incompatibility between reality and experimental work, we worked in the laboratory with real water from the company (almost 45 min from the laboratory).

Physicochemical analyzes

Conductivity, pH, TDS, salinity, and temperature

For measuring conductivity, pH, TDS, salinity, and temperature, a conductivity meter AH4400 was used.

COD measurement

Chemical oxygen demand (COD) represents the oxygen consumption by strong chemical oxidants to oxidize organic and mineral water. It allows assessing the pollution load of wastewater. Assessing the oxygen quantity (mg l^{-1}), used by the oxidation reactions, for the measurement of the reactants residue after 2 h. Oxidation is performed hot, in an acid medium, in the presence of an excess of oxidant. In a tube COD reagents, 2 ml of distilled water, boiling at 532 ± 2 K for 2 h, and after cooling we read the COD value at the colorimeter.

Measurement of BOD5

The biochemical oxygen demand over 5 days (BOD5) represents the oxygen amount required by microorganisms to oxidize (degrade) the total organic substance of water maintained at 293 ± 2 K and in the dark for 5 days. To measure this parameter, it firstly measured the oxygen concentration in a sample of water and repeated this measurement 5 days later. So, BOD5 represents the difference between the two concentrations.

Ion chromatography

To determine the inorganic anions in water, Thermo Scientific Dionex DX-120 and Thermo Scientific Dionex DX-500 Ion Chromatography Systems were used. So, the

Dionex DX-120 is a dedicated ion chromatography; the Dionex DX-500 is a modular system. For several analyses, 1000 mg l⁻¹ standard solutions are available from Thermo Scientific and other commercial sources. When these solutions are not available, 1000 mg l⁻¹ standards can be prepared by dissolving the appropriate amounts of the corresponding mass in 1000 ml of deionized water.

Microbiological study

The medium used is a solid medium where the culture medium of TSA (Tryptic Soy Agar, Difco, Detroit, MI, USA). The inoculation is at 310 ± 2 K for 18–24 h in the dark.

Electrochemical study

A conventional three-electrode system assembly with copper working electrode, Ag/AgCl electrode, and platinum electrode was used for electrochemical measurements. The chemical composition of copper is summarized in Table 1. The copper coupons were embedded in epoxy resin leaving 4.52 cm² cross-sectional areas exposed to the corrosive medium for electrochemical experiments. Prior to each experiment, the copper substrates were abraded consecutively with a series of emery papers (from 100 to 1200 grit), and then they were cleaned with acetone, washed with distilled water, and dried in hot air.

Prior to each electrochemical measurement, the working electrode was immersed in aggressive solution for 1 h at open circuit potential (E_{OCP}) to reach an almost steady state. Subsequently, EIS measurements were performed at the E_{OCP} in the frequency range from 100 kHz to 0.01 Hz using sinusoidal AC perturbation with an amplitude of 5 mV. The EIS data were analyzed and fitted by EC-Lab software. At last, polarization experiments were performed by changing the electrode potential automatically from negative values to positive values versus E_{OCP} using a potentiostat/galvanostat type PGZ 100, with a scan rate of 1 mV s⁻¹. All measured potential values were referred to the Ag/AgCl electrode. The same experiment was carried

out three times to guarantee a favorable reproducibility. To evaluate corrosion kinetic parameters, a fitting by Stern-Geary equation was used (Ben Amor 1999). The test solution was thermostatically controlled at 298 ± 2 K in air atmosphere.

Scanning electron microscope and X-ray diffraction analyses

To investigate the morphology and composition of the copper surfaces, the specimens were examined using a scanning electron microscope (SEM; JOEL JSM-5500) equipped with EDAX analyzer. Indeed, the phase present in the specimens was determined over the 2θ scale range from 20° to 90° using a Philips X-ray diffractometer X'Pert MPD.

Results and discussion

Characterization of make-up water

Moroccan industry of aluminum, copper, and zinc used water of the foundry MAC/Z Company of Skhirat/Morocco, where its chemical composition is given in Table 2. It is shown that this water contains the elements responsible for corrosion such as Cl⁻ ions and dissolved oxygen and the elements responsible to scale formation such as Ca²⁺, Mg²⁺, HCO₃⁻ ions. It is noted also the presence of sulfates responsible to corrosion and the development of microorganisms such as sulfate-reducing bacteria. So, Enning et al. indicated that the iron corrosion in anoxic environments (e.g., inside pipelines) is largely influenced by microorganisms, in particular sulfate-reducing bacteria (SRB). The process is characterized by the formation of black crusts and metal pitting. The mechanism is usually explained by the corrosive character of the formed H₂S and scavenges of 'cathodic' H₂ from the chemical reaction of iron with H₂O (Enning et al. 2012). For this, we have characterized this water for the development of the above problems.

Table 1 Chemical composition of copper

Elements	Zn	Pb	P	Mn	Fe	Ni	Si	Mg
Wt%	0.0031	0.0022	0.0008	<0.0004	0.0022	0.0054	<0.0005	0.0002
Elements	Cr	Te	As	Sb	Cd	Bi	Ag	Co
Wt%	<0.0003	0.0073	<0.0002	<0.0005	<0.0002	<0.0005	0.0014	<0.0010
Elements	Al	S	Zr	Au	B	Ti	Se	Cu
Wt%	<0.0005	<0.0002	<0.0003	<0.0005	<0.0004	<0.0002	<0.0002	99.976

Table 2 Physicochemical characterization of make-up water used in Moroccan industry

Elements	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	NO ₃ ⁻	PO ₄ ³⁻	F ⁻	Dissolved O ₂
Conc. (mg l ⁻¹)	300	130	284	0.7	0.1	0.77	6.85
Elements	NO ₂ ⁻	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	NH ₄ ⁺	TDS
Conc. (mg l ⁻¹)	3.7	80	67	193	7	0.1	874
Salinity	COD	BOD ₅		Conductivity		T	pH
0.88/1000	68.7 (mg l ⁻¹ O ₂)	26 (mg l ⁻¹ O ₂)		1803 μS cm ⁻¹		305 K	8.2

Evaluation of corrosion, scale, and biofiling of make-up water

Evaluation of corrosion and scale of make-up water

Predicting of scale formation

The scale and corrosion phenomenon are qualitatively predicted using various indices, namely the Langelier Saturation Index (LSI), the Ryznar Stability Index (RSI), and the Puckorius Scaling Index (PSI) (Langelier 1936; Ryznar 1944; Puchorius and Brooke 1988; Harris and Marshall 1981), which depend upon water parameters. So, the LSI is an indicator of the scale potential of cooling water. Thus a negative LSI indicates no potential to scale; the water will dissolve CaCO₃, while a positive value indicates CaCO₃ precipitation. In addition, an RSI >6 indicates corrosion while RSI <6 indicates scale formation. In addition, the PSI has the same indication as RSI. In fact, we have calculated the LSI and RSI at different temperature ranges from 295 to 335 K. This choice of temperature range based on those water temperatures can reach 313 K in a Moroccan cooling water system. Table 3 presents the obtained results at different temperature values. It was noted that all the Langelier Saturation Index (LSI) values were positive, which justified the formation of calcium carbonate. In addition, the Ryznar Stability index (RSI) value predicts that the sample at 295 K was under threat of corrosion and light scale. At the temperature range from 305 to 335 K, the RSI values changed in the range from 5 to 7, which means and predicts that the water is scaling and slightly corrosive.

However, these findings can be explained by the large amount of dissolved oxygen diffusing, which increases the amount of hydroxyl HO⁻ formed by two electrochemical reactions:

Table 3 Hardness of the used make-up water at different temperature [10,11]

Temperature (K)	pH _s	LSI	RSI	Scale conditions
295	7.7	0.48	7.2	Slightly scaling and corrosive
305	7.5	0.69	6.8	Scaling and corrosive
315	7.3	0.88	6.4	Scaling and slightly corrosive
325	7.1	1.1	6.1	Scaling and slightly corrosive
335	7	1.2	5.7	Slightly scaling and corrosive

However, the HO⁻ ions formed at the electrode surface induce an increase in local pH, causing precipitation of calcium carbonate (Ketrane et al. 2009). In addition, the chemical reaction causing the precipitation of calcium carbonate was widely promoted by temperature by the carbon dioxide release and thus accelerates the scale formation. There was little or no scale on cold water pipes. In contrast, at hot water systems the scale was formed. In fact, we noted an increase in the hardness of water with temperature. In order to confirm these results, we have conducted an experimental study using ion chromatography and spectroscopic analyzes.

Dosage of Ca²⁺ ions by ionic chromatography

To confirm previous theoretical results, we have evaluated the free Ca²⁺ concentrations in the solution before and after immersion of the copper substrate for 24 h at 323 K by ion chromatography. The obtained results are shown in Table 4, which indicates that the Ca²⁺ ion concentration in the solution decreases remarkably from 80 to 55 ppm, indicating the formation of the scale at the electrode surface. In addition, the observation of the electrode surface with the eye (Table 4) indicated that the surface is covered by a distinct purple corrosion and scale products layer. To ensure the scale and corrosion character of the studied water, qualitative and quantitative analyses with SEM/

Table 4 Free ions Ca^{2+} concentrations before and after immersion of copper substrate in make-up water for 24 h at 323 K

	$[\text{Ca}^{2+}]$ (ppm)	Surface state
Water before test	80
Water after 24 h of immersion at 323 K	55

EDAX analysis under the same conditions were carried out.

SEM and X-ray diffraction analyses

The evolution of surface states of copper using SEM analysis was carried out after 24 h of immersion at 323 K. Figure 1a shows the electrode surface of copper before any attack. It is shown that the surface was clean and homogeneous. However, Fig. 1b shows the state surface after 24 h of immersion at 323 K. It is noted that the apparition of a thick layer of products reflected the development of a thick film on the electrode surface. In fact, this layer was heterogeneous and exhibits at least two colors, one black, which may be due to the presence of corrosion products, and the other white, which may be due to scale products. In fact, EDAX analysis (Fig. 2a) showed that the formed layer was composed of several elements such as magnesium, calcium, copper, carbon, and oxygen with a strong predominance calcium (13.05 wt%), carbon (44.67 wt%), and oxygen (28.45 wt%). This result confirmed that the formed layer was composed of corrosion and scale products. It is also remarked the appearance of a sulfur peak (0.64 wt%) which can be indicated the development of sulfate-reducing bacteria, such as found by Enning et al. when they studied the marine sulfate-reducing bacteria on iron corrosion under electro-conductive biogenic mineral crust (Enning et al. 2012). In addition, the development of Cu_2S is the primary surface process on copper specimens where its corrosion protection properties improve by bio-film growth, which becomes less sensitive to Cl^- attack (Huttunen-Saarivirta et al. 2016).

Figure 2b shows the XRD analysis of the copper surface after 24 h of immersion in make-up water at 323 K. It is shown that the formed layer of corrosion products was composed of copper oxides such as cuprites (Cu_2O). The same results were found by other authors when they studied the copper corrosion under biotic and abiotic conditions in anoxic ground water (Huttunen-Saarivirta et al. 2016). In fact, their experiments were carried out in acid-washed ethanol (70%) sterilized vessels of the volume of 12 l that were essentially gas tight. Prior to the experiments, the ethanol-sterilized specimens and the electrodes were placed aseptically in the vessels, which were first flushed with N_2 to remove oxygen and then filled with anoxic artificial groundwater. This study included two vessels: one was made biotic by adding 50 ml of enrichment culture of sulfate-reducing bacteria (SRB) and the other abiotic, which was tested as such (Huttunen-Saarivirta et al. 2016). Indeed, the accumulation of Cu_2O on the copper surfaces either alone (Eriksen et al. 1989; Bojinov et al. 2010; Bech-Nielsen et al. 2002; Trachli et al. 2002; Kosec et al. 2015; Sherif and Park 2005; Merkel and Pehkonen 2006) or with some CuCl (Merkel and Pehkonen 2006; Kear et al. 2004) was frequently reported with another suggestion (Kosec et al. 2015; Sherif and Park 2005; Merkel and Pehkonen 2006) that the formed CuCl may react more late with water to introduce Cu_2O .

However, the appearance of calcium carbonate peak with great intensity is also noted, indicating the formation of a thick layer of scale confirming the previously obtained results.

Fig. 1 SEM micrograph surface of copper (a) before immersion in make-up water solution (b and b') after 24 h of immersion in make-up water solution at 323 K

Bacterial study of the make-up water

In this study, we have determined the character of make-up water for the development of microorganisms according to the middle agar diffusion method on the middle Mueller–Hinton. The obtained results are shown in Fig. 3. The appearance of bacterial colonies after immersion of samples in make-up water is noted, indicating that this water develops bacterial colonization. The same results were obtained when they studied the antibacterial properties of the 316L-Cu SS before and after passivation (Zhao et al. 2016).

In addition, after identifying the problems encountered in the cooling water system of copper (scale, corrosion, and development of microorganisms), we investigated the effect of some operating parameters on the evolution of these problems.

Electrochemical corrosion evaluation

Figure 4a represents the potentiodynamic polarization curve of copper electrode in make-up water at 305 K. It is noted that the anodic current increases exponentially with

applied potential, indicating kinetic charge transfer. Then, the corrosion potential (E_{corr}) and corrosion current density (i_{corr}) which were obtained by using Stern–Geary equation (i_{corr} is $8.44 \mu\text{A cm}^{-2}$) indicated that used water has a corrosive character.

Therefore, the anodic reaction involved in this case is the copper oxidation:

In addition, a current inflection at potential of 0.2 V/Ag/AgCl may be attributed to the formation of CuO_2 and/or CuO layers, as shown by the above XRD spectra.

At the cathodic range, the main reaction was the dissolved oxygen reduction, according to the following reaction:

Beyond -1 V/Ag/AgCl , the reduction of the water takes place to produce hydrogen gas.

However, the copper can be migrated deep under particular drainage conditions or in a highly acidic environment and can therefore contaminate groundwater. In order to minimize the copper amount, a new biodegradable

Fig. 2 a EDAX, b XRD spectra for copper surface after 24 h of immersion in make-up water solution at 323 K

formulation was used (Elhousni et al. 2016). For this, we have studied the inhibition of corrosion, scale-forming, and microorganism development of copper in the Moroccan cooling water system by sodium gluconate (SG), cetyltrimethyl ammonium bromide (CTAB), and their mixture using electrochemical measurements coupled with scanning electron microscopy (SEM). It was found that the SG acts as a cathodic-type inhibitor and its inhibition is about 95% at 10^{-3} M and the CTAB acts as a mixed-type

inhibitor and its best inhibition is at 15 ppm. In addition, the synergistic effect of SG/CTAB study indicated that CTAB decreases the performance of SG from 95 to 88% and increases with immersion time.

In addition, Fig. 4b represents the Nyquist plot of copper in make-up water at the open circuit potential. It is shown that the obtained plot is an imperfect semicircle in the low-frequency region preceded by a straight line at high-frequency range. Generally, the high-frequency loop

Fig. 3 Results of the agar diffusion method on the *middle* Muller-Hilton for make-up water

was attributed to the adsorbed species (R_{ad} and C_{ad}) and the second loop at the low frequency was attributed to the resistance transfer charge (R_{ct}) and double layer capacitance (C_{dl}). The corresponding equivalent circuit fitted the impedance data is shown in the insert of Fig. 4b. Here, R_s is the solution resistance, R_{ad} is the resistance of the adsorbed species copper surface, and R_{ct} represents the charge transfer resistance. Q_{ad} and Q_{dl} are constant phase-angle elements (CPE), representing an adsorbed species capacitance (C_{ad}) and double-layer capacitance (C_{dl}), respectively.

However, the calculation of the current density i_{corr} from polarization resistance determined from the impedance diagram ($R_p = 8.07 \text{ k}\Omega \text{ cm}^2$) gives $6.63 \mu\text{A cm}^{-2}$. Therefore, the estimated value from the polarization curves is $8.44 \mu\text{A cm}^{-2}$. This difference was attributed to that the polarization resistance estimated from potentiodynamic polarization curves encompasses the charge transfer resistance and the resistance of the dissolved oxygen diffusion to the copper surface or the transportation of soluble cuprous chloride complexes from the copper surface to the bulk solution.

Operational parameter effect on scale formation

pH is a very important parameter that controls the scale formation and the corrosion character. In fact, water at pH below 7 can promote corrosion of metal pipes while at a high pH can lead to scale deposits in cooling water circuits. In our case, the pH value is about 8.2 conducted to the

Fig. 4 **a** Potentiodynamic polarization curve and **b** Nyquist plot combined with equivalent circuit used to fit the EIS data of copper in make-up water solution at $T = 305 \text{ K}$

scale formation such as mentioned above. For this, Fig. 5a presents the effect of the pH solution, by addition of NaOH or H_2SO_4 , on the scale formation by the determination of the free Ca^{2+} concentrations using ion chromatography. It is noted that at a pH level between 6.5 and 8.2, the free Ca^{2+} concentration remains almost constant. Thus, an increase of pH beyond 8.2 caused a remarkable decrease in the free Ca^{2+} concentration, indicating that the scaling process was intensified. In fact, the pH of the natural waters was generally between 6 and 8. At a pH range from 7 to 8, less than 2% of carbonates are in the form of CO_3^{2-} and H_2CO_3^* of the majority HCO_3^- (Mulford 1964). Lee and Ambrose observed that at a pH of 7.9, the formed scale was finer than that formed at pH 8.3, when they studied the effect of applied potential, fluid velocity, pH, and temperature on the calcareous deposit formation under impressed current cathodic protection (Lee and Ambrose 1986). They also found that the scale deposit depends

Fig. 5 Effect of **a** pH solution, **b** Cl^- , and **c** SO_4^{2-} ions concentration on the free Ca^{2+} concentration in the solution

primarily on interface pH, which was much higher than the electrolyte. Thus, the variation of bulk pH had little influence on the cathodic reaction rate, which was measured in terms of current, though $[\text{HO}^-]$ is in the reaction path for both oxygen reduction and hydrogen evolution reactions:

The fact that the cathodic current is mainly comprised of hydrogen evolution and oxygen reduction currents allows us to interpret the measured pH effect as the sum of the two corresponding parts. Therefore, the oxygen reduction reaction is diffusion-controlled at the potentials of their study. Therefore, variation in pH should not have any influence on oxygen reduction current, though $[\text{HO}^-]$ is in the reaction path of the oxygen-reduction reaction (Lu and Fabuss 1968). In contrast, hydrogen evolution is kinetically controlled. Therefore, a decrease in pH from 8.3 to 7.9 is expected to yield a slight increase in the hydrogen evolution current where its amount can be calculated from the relationship between current and over-potential. Indeed, in our case, the formed scale layer was thick (pH 8.2), in agreement with the obtained results by SEM.

However, as indicated in Table 1, the amount of chloride and sulfate ions were 300 and 130 mg L^{-1} , respectively. The presence of these ions with a high concentration leads to corrosion and bio-corrosion problems. So, Huttunen-Saarivirta indicated that in the presence of microorganisms (e.g., sulfate-reducing bacteria), the development of Cu_2S is the primary surface process on copper specimens, with its corrosion protection properties being regulated by the growth of bio-film. As compared to the two layers of Cu_2O that grow on the specimen surfaces in the absence of bacteria, Cu_2S films were essentially less susceptible for the Cl^- attack. They found that under abiotic conditions, the passivity breakdown by Cl^- ions resulted in the localized type of attack detected on the surfaces. This finding is the probable reason for an essentially higher corrosion rate than in the biotic system (Huttunen-Saarivirta et al. 2016). For this, we have studied the influence of chloride and sulfate ions on the scale formation, such as presented in Fig. 5b, c. It is noted that the free Ca^{2+} concentration decreases linearly with increasing of Cl^- and SO_4^{2-} ions. This finding can be explained by the formation of CaCl_2 and CaSO_4 on the metallic surface.

However, an electrochemical study of the scale process has shown that at different applied potentials, an increase in the chloride ions concentration resulted in the formation of a porous deposit. Indeed, according to the small size of the chloride ions, they can penetrate between the joints of the formed deposit (Ben Amor 1999).

In the other, the presence of sulfate ions caused the formation of a porous scale layer where its porosity is larger than that formed in the case of chloride ions (Ben Amor 1999).

Fig. 6 **a** Potentiodynamic polarization curves of copper in make-up water at different temperature, and **b** $\ln i_{\text{corr}}$ vs. $1/T$ plot used to calculate the Arrhenius slope

Operating parameters effect on corrosion

Effect of temperature solution

The corrosive medium temperature is an essential parameter in the operation of cooling water systems. It is considered one of the factors that may affect the substrate behavior in an aggressive environment. For this, the potentiodynamic polarization curves for copper in make-up water were carried out at different temperatures range from 305 to 335 K. The choice of this temperature range was justified by the fact that iron, copper, and their alloys used

in the cooling water systems where their temperature could reach 335 K (Amar et al. 2006). Figure 6a presents the obtained results. It is noted that the anodic and cathodic branches change in form with temperature, indicating a change in the behavior of copper in make-up water. This effect was attributed to the increase of the diffused oxygen quantity in the solution with temperature (Stern and Geary 1957). Table 5 showed that the current density increases with temperature, indicating an increase in the copper corrosion rate.

However, the corrosion rate versus temperature can be expressed by the Arrhenius equation:

$$i_{\text{corr}} = K \exp\left(-\frac{E_a}{RT}\right), \quad (8)$$

where i_{corr} is the corrosion current density (A cm^{-2}), K is the frequency factor, E_a is the activation energy of the copper corrosion reaction, R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), and T is the absolute temperature (K).

The obtained plot $\ln i_{\text{corr}}$ vs. $1/T$ is given in Fig. 6b. The obtained experimental curve corresponds approximately to a straight line and the E_a value can be obtained from its slope. The obtained value of E_a is $48.72 \pm 6.02 \text{ kJ mol}^{-1}$ (Table 5), which is greater than that obtained for copper in 0.5 M NaCl (17.9 kJ mol^{-1}), indicates the corrosion character of the studied water (Rahal et al. 2016).

Effect of pH solution

Figure 7 shows the Nyquist plots of copper in make-up water solution at different pH values. It is shown that the obtained Nyquist plots were composed of two loops, the first at a high frequency and the second at a low frequency range. Generally, the first was attributed to the adsorbed species at the metallic surface and the second was attributed to the charge transfer resistance (R_{ct}) and double-layer capacitance (C_{dl}). The proposed equivalent circuit is shown in the insert of Fig. 7 and the obtained electrochemical parameters are listed in Table 6. It is noted that both values R_{ct} and R_{ad} increase with pH. This effect can be explained by the formation of a pseudo protective film by the adsorption of corrosion (CuO_2) and scale (CaCO_3) products such as mentioned above and confirmed by XRD spectra.

Table 5 Electrochemical parameters of copper in make-up water solution at different temperatures

T (K)	E_{corr} (mV/Ag/AgCl)	I_{corr} ($\mu\text{A cm}^{-2}$)	β_c (mV dec $^{-1}$)	β_a (mV dec $^{-1}$)	E_a (kJ mol $^{-1}$)
305	−24.0	8.44	−190	100	48.72 ± 6.02
315	−88.6	26.50	−177	82	
325	−108.0	42.00	−192	79	
335	−95.0	48.00	−138	75

Fig. 7 Nyquist plots for copper in make-up water solution at different pH solution, combined with equivalent circuit used to fit the EIS data

Immersion time

Figure 8 shows Nyquist plots for copper in make-up water solution after different immersion times. The obtained diagrams show the presence of two semicircles. The first loop may correspond to the formation of corrosion and scale products on the metallic surface. The second loop was attributed to the charge transfer and double-layer capacitance. The analysis of these plots was performed with the proposed equivalent circuit presented in the insert of Fig. 8. This model was used in our previous works to

Fig. 8 Nyquist plots for copper in make-up water solution at different immersion times, combined with an equivalent circuit used to fit the EIS data

describe the behavior of copper and brass in cooling water solution, with or without inhibitors (Elhousni et al. 2016; El Bakri et al. 2016; Rochdi et al. 2014). In this model, R_s is the solution resistance, R_{ct} is the charge transfer resistance, Q_{dl} corresponds to the capacitance of the double layer, and the R_{ad} and the element Q_{ad} correspond to the film formation of corrosion and scale products. Actually, Q_{dl} and Q_{ad} represent constant phase elements (CPE) used in the place of capacitors to compensate for deviations from ideal dielectric behavior. These deviations were attributed the inhomogeneous nature of the electrode due to surface roughness, inhibitor adsorption, porous layer

Table 6 Impedance parameters of copper in make-up water solution at different pH, immersion time, and chloride ion concentration

Parameters	R_s $k\Omega\text{ cm}^{-2}$	C_{ad} $\mu F\text{ cm}^{-2}$	R_{ad} $k\Omega\text{ cm}^{-2}$	C_{dl} $\mu F\text{ cm}^{-2}$	R_{ct} $k\Omega\text{ cm}^{-2}$	R_p $k\Omega\text{ cm}^{-2}$
pH						
6.5	0.097	77	0.6	285	2	1.60
7.5	0.104	82	0.4	244	3.5	2.90
8.3	0.123	50	1	140	7.2	8.07
9	0.120	48	1.2	188	5.5	5.50
10	0.114	44	1.4	122	7	7.30
Time (h)						
1	0.123	50	1	140	7.2	8.07
36	0.141	106	5	279	16.2	21
48	0.124	68	11.5	84	20.2	32
300	0.130	223	1.9	13	36.4	38
$[Cl^-]$ (ppm)						
400	0.123	50	1	140	7	8
600	0.101	44	2	255	6	8
800	0.080	51	1	284	6	7
1000	0.058	60	1	305	2	3
1200	0.057	75	1	344	2	2

Fig. 9 Nyquist plots for copper in make-up water solution at different chloride ions, combined with equivalent circuit used to fit the EIS data

formation, etc. The obtained electrochemical parameters are listed in Table 6, where R_p is the total polarization resistance of copper in the solution (R_p is the sum of R_{ad} and R_{ct}). It is noted that R_{ct} and R_{ad} increase with immersion time to reach 38 and 11 $k\Omega\text{ cm}^2$, respectively. These results explained why the curve's nature changes with the times.

Effect of Cl^- ions

Figure 9 shows the Nyquist diagrams obtained from copper in make-up water solution at different concentrations of Cl^- ions. The obtained plots were composed of two loops, one at high frequency, which corresponds to the formation of corrosion and scale products on the copper surface. The other loop at low frequency was mainly attributed to the charge transfer and double-layer capacitance. So, the analysis of these diagrams was performed with the proposed equivalent circuit presented in the insert of Fig. 9 and the obtained parameters are listed in Table 6. It is noted that the R_{ct} decreases with an increase of chloride ions. The best decrease was observed at 1000 and 1200 ppm. In addition, generally no change was observed for R_{ad} . However, the decrease of R_p was mainly due to the decrease of R_{ct} with the rise of chloride ions.

Conclusions

Electrochemical measurements coupled with SEM/EDAX and X-ray diffraction analyses were used to investigate corrosion and scale process of copper in the Moroccan industrial cooling water system. It is shown that this water

contains several elements responsible for corrosion and scale formation, such as Cl^- , Ca^{2+} , Mg^{2+} , HCO_3^- ions. These findings were confirmed by EDAX and XRD analyses. In fact, the EDAX and XRD analyses indicated that the major corrosion and scale products were CuO_2 and CaCO_3 , respectively. In addition, the middle Mueller–Hinton test for the development of microorganisms indicated the presence and colonization of microbial species in make-up water. Finally, it was found that the scale rate increases with pH, temperatures, and the presence of chloride and sulfide ions. On the other hand, electrochemical measurements indicated that the increase of temperature and chloride ion concentrations cause an increase in the corrosion rate. Additionally, the electrochemical impedance spectroscopy showed that the polarization resistance of the copper increases with pH and immersion time, which can be explained by the formation of a protective layer composed of corrosion and scale products.

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Compliance with ethical standards

Conflict of interest All of the authors have declared no conflicts of interest.

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