

The Effect of Some Key Changes in the Chemistry of Water in Relation to Copper and Brass Corrosion Control

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Abstract. Corrosion means the degradation of the metals or their alloys, under the action of chemical or electrochemical agents from the environment. The complex corrosion phenomenon has a destructive action, generating undesirable economic consequences: metals and labor losses, appreciable reduction in the lifetime of various metal constructions, insecurity in the operation of industrial machinery. Under the current conditions of accelerated growth in the production of material goods, one of the most important issues is the economy of raw materials and materials, energy and labor force. Copper, having a purity of over 99%, is used in the manufacture of gas and water pipes, roofing materials, utensils and ornamental objects. Brass is used in the manufacture of flexible tubes, pipes, coils, cartridges, various electrochemical parts, jewelry, etc. The aim of this research work was to evaluate the corrosion resistance of copper and brass in various solutions: with different chloride ions as 35 g/L NaCl, waste water and tap water. The corrosion behavior of copper and brass was analyzed by electrochemical methods, such as: open circuit potential (OCP), electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV). Pure copper exhibits more noble potential values than its alloy (brass), according to the evolution of free potential in all tested solutions. After performing the electrochemical assays, ex-situ investigations, by optical microscopy, were made and the results confirm that the chloride ions affect the corrosion behavior of copper and brass. Corrosion of materials is a very important process to consider when choosing a material that has to operate in a specific environment.

1. Introduction

Copper and brass are materials especially used in cooling water systems, air conditioning systems and drinking water systems because they have good corrosion resistance and high thermal conductivity [1-6].

In addition to excellent conductivity, copper has ideal mechanical properties at low, ambient and high temperatures, it is easy to manufacture or mold and can be easily machined. It has excellent resistance to oxidation and corrosion [1, 2]. Copper is the fifth most widely used metal in the world to be useful in pure or alloy form. The most commonly used copper alloys are brass, copper-nickel and bronze. The presence of corrosion products on the copper surface leads to a decrease in the performances of a system built with this material [5].

Copper has a low corrosion rate. The good corrosion resistance of copper and its alloys is due to the development of protective layers of degradation products that diminish the attack rate [6].



Brass is copper alloyed with zinc. In industry are used alloys with up to 50% Zn. Brass with 30-32% Zn content possess good plasticity characteristics [2]. Brass is an alloy tough and easy to be processed used to make pipes, valves, fittings objects [3].

When chloride ions are present in aqueous solutions, copper and brass are susceptible to pitting corrosion [7].

The aim of this work is to evaluate the corrosion behavior of copper and brass in 35 g/L NaCl solution, tap water from Galati water plant and a low concentration waste water from water distribution system in Galati. The corrosion behavior of copper and brass was evaluated using electrochemical methods: open circuit potential (OCP) and electrochemical impedance spectroscopy (EIS) and the surfaces of analyzed samples, before and after the corrosion assays, were evaluated using the Optical Microscope OPTIKA XDS3 MET.

2. Experimental procedures

2.1. Materials and methods

The chemical composition of the tested samples was Cu-99.97% for copper and for brass: Cu-57.8%, Zn-39.02%, Pb-2.99%, Fe- 0.19%.

In order to assess the corrosion behavior, the analyzed samples were connected with copper wire for electrical contact and insulated with epoxy resin, leaving a working area of 2 cm². The working area was cleaned with HNO₃ and rinsed with distilled water before the corrosion assays.

For the electrochemical measurements it was used a conventional three-electrode cell, consisting of: a working electrode made of copper or brass, a Pt-Rh grid that serve as auxiliary electrode and an Ag/AgCl reference electrode (with saturated KCl solution, E= +199 mV vs. standard hydrogen electrode–SHE). The corrosion experiments were done using a potentiostat / galvanostat PGZ 100 and the experimental data were recorded with VoltaMaster4 software.

Corrosion assays were performed for copper and brass in three different electrolytes: tap water from Galati water plant, alow concentration waste water from water distribution system in Galati and 35 g/L NaCl aqueous solution. The chemical composition of these electrolytes, by point of view of chloride concentration, is shown in Table 1.

In Table 2 are shown the physico-chemical characteristics of these electrolytes which have been measured with a multi-parameter analyzer CONSORT C 533.

Before and after the corrosion assays, the surfaces of analyzed samples of copper and brass were analyzed using the optical microscope OPTIKA XDS-3MET in order to evaluate the corroded area.

Table 1. The chemical composition of the electrolytes used in corrosion assays.

Electrolytes	NaCl solution	Tap water	Waste Water
Chloride ions (Cl ⁻)	21.27 g /L	0.0360 g /L	0.801 g /L

In Table 2 are shown the physico-chemical characteristics of these electrolytes which have been measured with a multi-parameter analyzer CONSORT C 533.

Table 2. Electrolytes physico-chemical parameters.

Solution type	pH	Conductivity [mS]	Salinity [‰]
NaCl solution	5.71	41.2	26.2
Tap water	7.52	1.04	0.5
Waste water	6.07	6.57	3.6

The solutions used for corrosion tests are different concentration of chloride ions and differ slowly in pH value, which are the key components in an aggressive corrosive environment.

3. Results and discussion

3.1. Open circuit potential

The corrosion tests began with monitoring the evolution of open circuit potential after the immersion of copper and brass into the electrolytes. This free potential varies with time due to the oxidation trend of the samples surfaces.

From Figure 1 (a) it can be seen that copper immersed in 35 g/L NaCl aqueous solution showed a small shift tendency of the free potential to the more negative (active) direction having at the end of 60 minutes the value of -235.81 mV vs. Ag / AgCl, compared to the initial value of free potential at the immersion time of -233.81 mV vs. Ag / AgCl.

On the other hand, for the copper immersed in waste water from Figure 1 (a) it can be observe that, the open circuit potential show a slow shift in the more positive direction, from +0.44 mV vs. Ag/AgCl up to +18.07 mV vs. Ag/AgCl at the end of monitoring period.

For the copper sample immersed in tap water, from Figure 1 (a) it can be seen a slow shift of open circuit potential in the more positive direction, having at the end of the monitoring period a value of -36.06 mV vs. Ag/AgCl, compared with the initial immersion time value of -73.31 mV vs. Ag/AgCl.

Comparing the evolution of OCP recorded for copper in all three solutions (Figure 1 (a)) it can be observed that due to the high concentration of chloride ions in 35 g/L NaCl aqueous solution, the immersed sample react with the chloride ions and the passive layer formed at material-electrolyte interface is dissolved immediately.

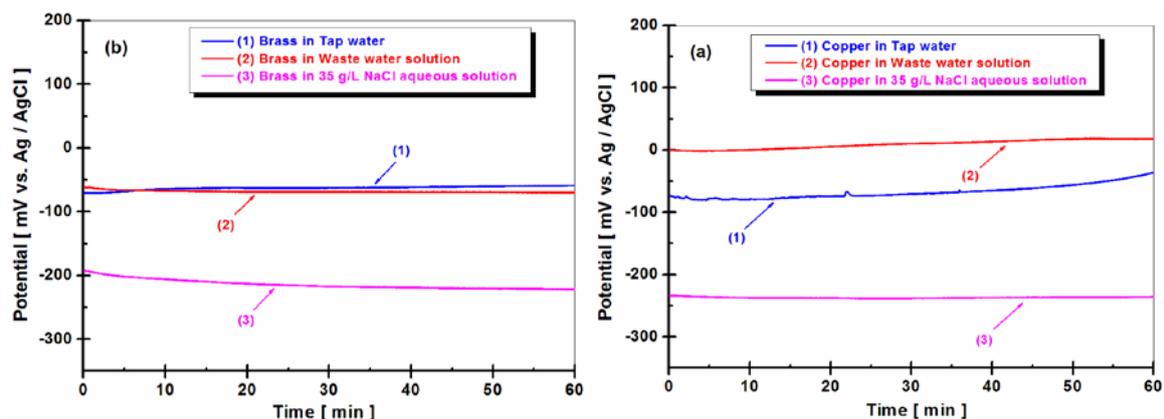


Figure 1. Open circuit potential (OCP) recorded for (a) copper and (b) brass immersed in 35 g/L NaCl solution waste water and tap water for 60 minutes.

For the copper samples immersed in artificial waste water or tap water, the free potential shows a shift tendency, to more noble values, that could be explained by the fact that at the material-electrolyte interface a passive layer is formed and protects the copper substrate against the aggressiveness of chloride ions from the electrolytes.

The open circuit potential recorded for the brass sample immersed in 35 g/L NaCl aqueous solution presented in Figure 1 (b) shows a shifted tendency to more negative value from -192.25 mV vs. Ag/AgCl at the initial immersion time to the value of -221.56 mV vs. Ag/AgCl at the end of the measurement.

For brass sample immersed in waste water, the open circuit potential exposed in Figure 1 (b) shows a very small shifted value to more negative value of free potential from -60.87 mV vs. Ag/AgCl at initial immersion time to -69.43 at the end of measurement. For brass immersed in tap water, the open circuit potential shows a shifted trend to more positive (noble values), from -70.43 mV vs. Ag/AgCl at initial immersion time to -58.62 mV vs. Ag/AgCl at the end of the monitoring period.

The shifted values of free potential during immersion time of brass confirms the formation on the brass surface of a more stable passive oxide layer in tap water solution while the shifted trend to more

negative values of brass in waste water and 35 g/L NaCl aqueous solution indicates a higher instability and a degradation of the passive film formed on brass surface in these solutions due to higher concentration of chloride ions.

3.2. Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) is a non-destructive method used to investigate the corrosion performance metals that are exposed to an aqueous environment. Experimental impedance is the result of the serial binding of resistances and capacitances.

The electrochemical impedance spectroscopy measurements were performed to characterize the corrosion behaviour of copper and brass immersed in NaCl solution, tap water and waste water solutions.

The EIS spectra were recorded in the frequency range from 100 kHz to 10 mHz, with amplitude of the sine-wave signal of 10 mV. The impedance data recorded for copper and brass immersed in all three solutions were displayed in the form of a Bode plots in (Figure 2 and Figure 3).

The EIS spectra were fitted to equivalent circuit (Figure 4) using ZView 3.4f software and the quality of the fitted results was evaluated with the chi-square value that was lower than 10^{-3} .

Figure 2 (a) and (b) shows the EIS results, in the form of the Bode plots for copper immersed in three electrolytes after 1 h of immersion.

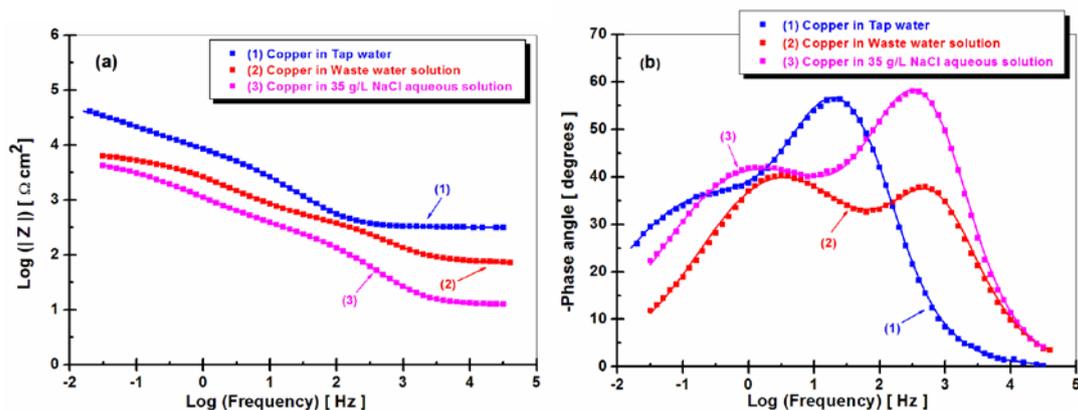


Figure 2. Bode impedance plots of copper immersed in: (1) tap water (2) waste water and (3) NaCl solution. (a) impedance modulus vs. frequency plots and (b) phase angle vs. frequency plots. The plain symbols represent the experimental data and the continuous lines represent the fitted results.

From the Bode plots between $\log |Z|$ and $\log (f)$ from Figure 2 (a), it could be observed that the curve corresponding to copper immersed in tap water displayed a higher impedance modulus over the entire frequency range. This remark indicates a nobler electrochemical characteristic for copper immersed in tap water as compared with copper immersed in waste water and NaCl solution. The corrosion attack is much more aggressive for copper immersed in waste water and NaCl solution as compared with copper immersed in tap water which could be easily detected by small phase angle in the lower-frequency ranges, as it is shown in Figure 2 (b)). This behaviour can be explained by the lower chloride ions concentration in tap water as compared with the waste water and NaCl solution.

Figure 3 (a) and (b) shows the EIS results, in the form of the Bode plots for brass immersed in three electrolytes after 1 h of immersion time.

From the Bode plots showed in Figure 3 (a) and (b) it is observed a similar behaviour for brass immersed in tap water as it was observed for copper immersed in the same solution. The corrosion attack is much more aggressive for brass immersed in waste water and NaCl solution as compared with brass immersed in tap water. Also here, the higher concentration of chloride ions from waste

water and NaCl solution is responsible for more pronounced corrosive attack.

For the copper and brass electrodes immersed in NaCl aqueous solution, tap water and the waste water solution, an equivalent electrical circuit is proposed and shown in Figure 4.

The proposed electrical circuit was used to fit the EIS experimental spectra where R_1 was designated as the resistance of the electrolyte, CPE_1 and R_2 are the constant phase element and the polarization resistance respectively of the formed oxide layer on the copper and brass surfaces during oxidation of the base metal.

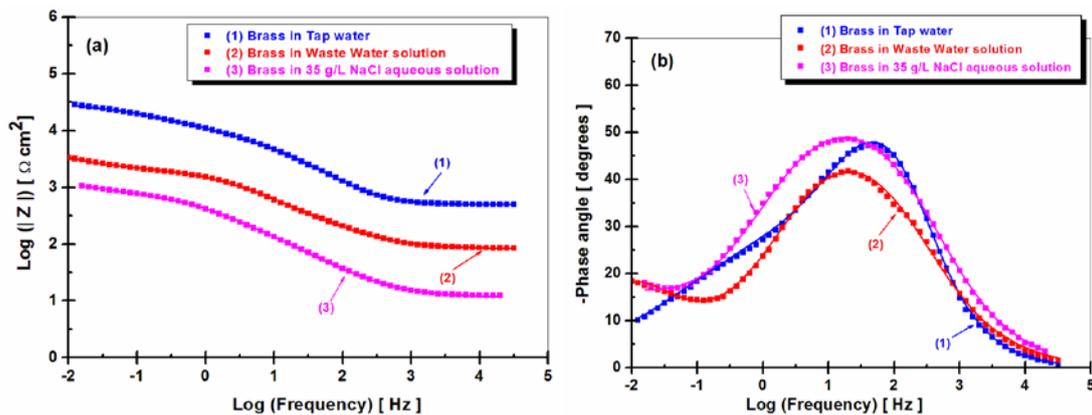


Figure 3. Bode impedance plots of brass immersed in (1) tap water, (2) waste water and (3) 35 g/L NaCl: (a) impedance modulus vs. frequency plots and (b) phase angle vs. frequency plots. The plain symbols represent the experimental data and the continuous lines represent the fitted results.

CPE_2 and R_3 designate the constant phase element and the resistance respectively of the base metal.

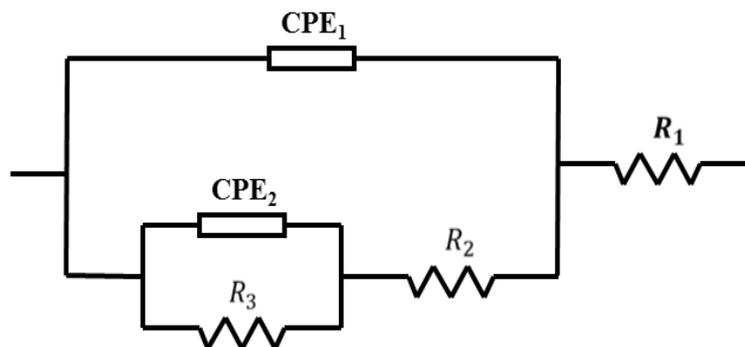


Figure 4. Schematic representation of the equivalent electrical circuit used to fit and simulate the experimental data of the electrochemical impedance spectra recorded for copper and brass surfaces in three aggressive environments.

Following the fitted electrochemical impedance spectroscopy diagrams the specific polarization resistance values for both surfaces in the three corrosive environments were obtained. For the copper electrode immersed in waste water solution the specific polarization resistance value is approximately 7231 kohm cm^2 . On the other hand, for the brass electrode immersed in waste water, the specific polarization resistance value is about 5450 kohm cm^2 .

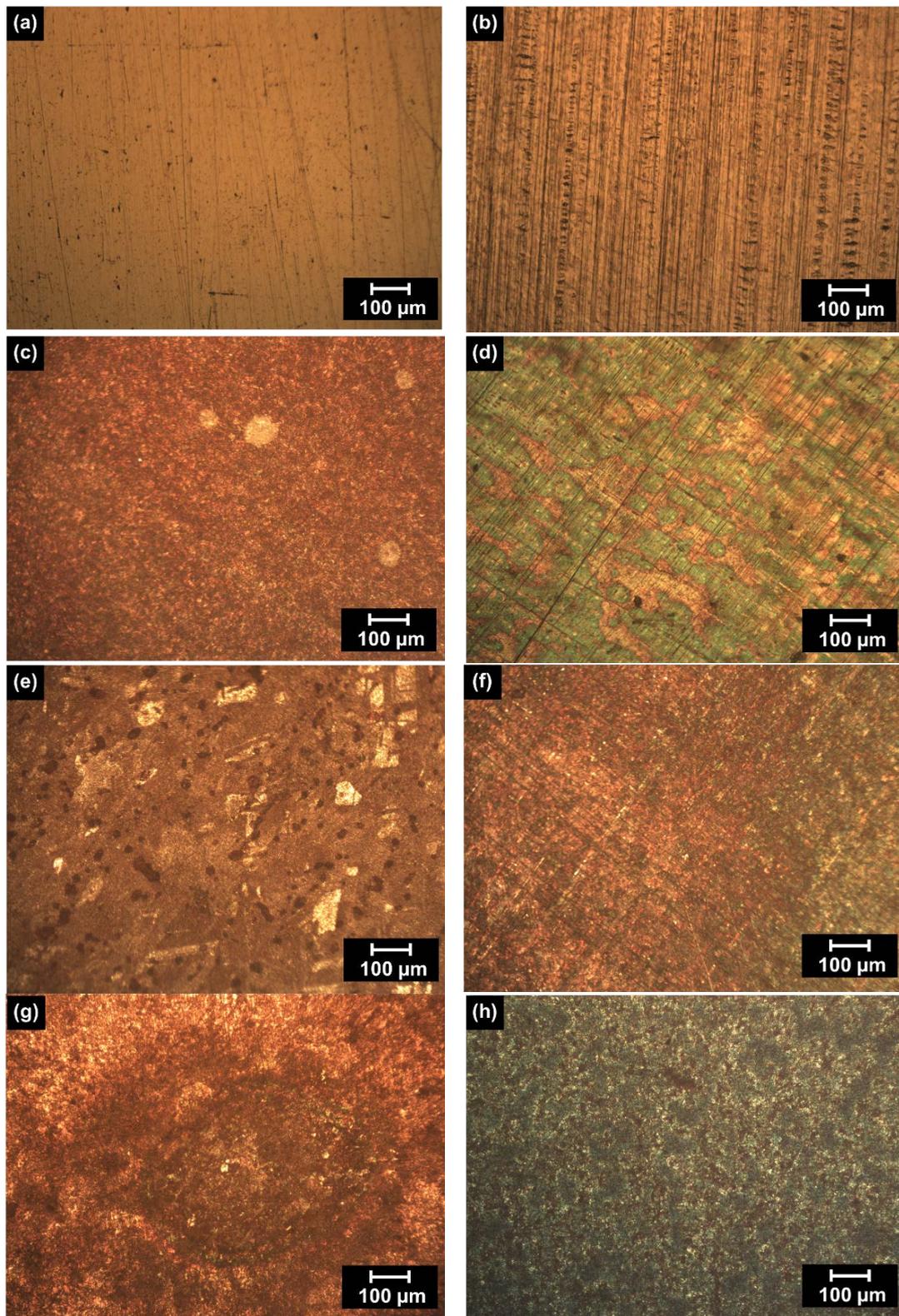


Figure 5. Optical microscopy images recorded before the corrosion assays for (a) brass and (b) copper. The micrographs after the corrosion assays in tap water for (c) brass and (d) copper. After the corrosion assays in waste water for (e) brass and (f) copper. After the corrosion assays in NaCl aqueous solution for (g) brass and (h) copper.

The specific polarization resistance determined using the proposed equivalent circuits shows that for the copper electrode immersed in tap water the specific polarization resistance value is about 69297 kohm cm². On the other hand, for the brass electrode immersed in the tap water the specific polarization resistance value is approximately 58837 kohm cm².

The specific polarization resistance was determined using the proposed equivalent circuit and shows that for the copper electrode immersed in NaCl aqueous solution, the specific polarization resistance value is 6348 kohm cm². On the other hand, for the immersed brass electrode of NaCl the specific polarization resistance value is about 3330 kohm cm².

3.3. Optical Microscopy analysis before and after corrosion

Copper and brass surfaces were investigated using the optical microscope before and after the corrosion test in NaCl aqueous solution, tap water and waste water in order to analyze the corrosive effects on their surfaces and the recorded images are shown in Figure 5.

Before the electrochemical assays, on the copper and brass surfaces can be observed lamination tracks, Figure 5 (a) and (b). The copper and brass surfaces, Figure 5 (c) and (d) immersed in tap water, on the analyzed surfaces a few corrosion spots (localized corrosion) can be identified due to the small quantity of chloride ions in the electrolyte.

For the copper and brass samples immersed in artificial water, Figure 5 (e) and (f) and for immersion in NaCl solution, Figure 5 (g) and (h) a generalized corrosion can be identified. Following the increasing concentration of chloride ions into the electrolytes, the corroded areas increase also on copper and brass surfaces.

The optical micrographs confirm the observed corrosion behaviours of copper and brass from electrochemical measurements as open circuit potential and electrochemical impedance spectroscopy.

4. Conclusions

The aim of this paper was to evaluate the corrosion resistance of copper and brass in various solutions, with different chloride ions, such as 35 g/L NaCl solution, waste water and tap water.

According to the evolution of open circuit potential of copper in all tested solutions, it can be observed that due to the high concentration of chloride ions in 35 g/L NaCl aqueous solution, the immersed sample react with the chloride ions and the passive layer formed at material-electrolyte interface is dissolved immediately. On the other hand, copper samples immersed in artificial waste water or tap water, the free potential shows a shift tendency, to more noble values, that could be explained by the fact that at the material-electrolyte interface a passive layer is formed and protects the copper substrate against the aggressiveness of chloride ions from the electrolytes.

The electrochemical impedance spectroscopy measurements reveals that the copper and brass samples immersed in tap water show a higher impedance modulus in comparison with the brass samples immersed in waste water and NaCl solution.

The specific polarization resistance shows that for the copper electrode immersed in NaCl aqueous solution, the specific polarization resistance value is 6348 kohm cm². On the other hand, for the copper electrode immersed in waste water solution the specific polarization resistance value is approximately 7231 kohm cm² and for the copper electrode immersed in tap water the specific polarization resistance value is about 69297 kohm cm².

The specific polarization resistance shows that for the brass electrode immersed in NaCl aqueous solution, the specific polarization resistance value is 3330 kohm cm². On the other hand, for the brass electrode immersed in waste water solution the specific polarization resistance value is approximately 5450 kohm cm² and for the brass electrode immersed in tap water the specific polarization resistance value is about 58837 kohm cm².

From the analysis of optical images, it can be observed that the increasing the chloride ions content, the analyzed surfaces present larger corroded area. Also, it can be observed that the copper and the brass samples present a generalized when were immersed in electrolytes with an increased quantity of chloride ions.

The electrochemical impedance spectroscopy measurements reveal that a nobler electrochemical characteristic is achieved for copper immersed in all tested solutions as compared with brass, which describes a more protective passive film. The specific polarization resistance is higher for copper in all tested solutions.

5. References

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Acknowledgements

This work was supported as part of the research projects and expertise of Competences Center for Interfaces - Tribocorrosion and Electrochemical Systems (CC-ITES) from Dunarea de Jos University of Galati, Romania. www.cc-ites.ugal.ro.