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Electrochemical Corrosion on Metals in Soil

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Abstract

Petroleos Mexicanos and the Federal Electricity Commission parastatals of Mexico, carry out activities of great diversity in metal infrastructure buried throughout the country. Therefore, it is considered important to evaluate the corrosion on the soil of the oil zone of Poza Rica, which is home to many piping systems to transport oil and high-voltage transmission towers. The electrochemical evaluation of corrosivity was made on carbon steel coupons, as well as on coupons made of copper, aluminum and zinc, with techniques of Polarization Resistance (RP), Potentiodynamic Polarization Curves (CP) and Electrochemical Impedance Spectroscopy (EIS). Grain size, moisture content, resistivity, chlorides, pH and redox potential was determined in order to characterize the electrolyte. Carbon steel has an increased corrosion rate due to the minor protection delivered by the corrosion coating formed. However, for materials such as Cu, Al, Zn, the corrosion products (identified by X-Ray Diffraction) form a very thin protective coating that achieve a seal protecting the substrate from surface soil aggressiveness.

Corrosivity, soil, electrochemical techniques

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Introduction

A large portion of the metal infrastructure (pipelines for water, gas or oil, metal cables for communications, tanks for fuel storage containers of toxic waste, concrete structures with steel reinforcement), is buried, where the aggressive environment is the ground with their physicochemical properties and other weather-related parameters [1, 8-9]. The study of corrosion in soils is important for the industry given the fact that most steel structures must rest on the ground or be buried, to fulfil mechanical, economic and security needs; these structures are then subject to a corrosion process where in some cases can be very complex [1-3]. This corrosion, in these structures, is very common and poses a problem for optimal fluid transport, for the generation of pitting and loss of mechanical properties that cause leaks and can even cause fatalities, millions in losses by waste of raw materials and pollution in areas where spills of the transported materials happens this way. Prevention of these failures can be done effectively if the corrosion mechanism involved is known, the way it is carried out and the evaluation of their electrochemical behavior [2, 9].

With variable moisture content, salt and decomposition organic matter, the soil is the most complex electrolyte of all that can be found; It is a heterogeneous environment where many variations occur in the corrosion rate of metals [1-4]. The presence of moisture in the soil makes possible the existence of an electrolyte film on the metal surface, whose aggressiveness depends on the soil type and degree of contamination (decomposition organic matter, bacterial flora).

Thus, the soil can form a more complex electrolyte on the metal surface with different degrees of aggressiveness -a necessary element for the development of the corrosion process and its electrochemical nature [9]. The diversity of soil types causes a considerable variation of their chemical and physical characteristics that influence the corrosive aggressiveness on metal structures. The land, with its heterogeneities, and the metal with its surface imperfections, originate on the metal surface anodic and cathodic areas. The soil in contact with the metallic material acts as electrolyte, due to moisture and soluble salts conteined. Associated to the electrochemical corrosion process, there is always an anodic metal oxidation reaction and a cathodic reaction comprising the reduction of O_2 in neutral or alkaline media, or reduction of protons (H^+) in an acid medium [10].

The soil corrosive activity is determined by its acidity, moisture, salts and oxygen, bacterial activity, texture and electrical resistance. The acidity is high in wet and marshy soils and low in dry and ventilated ones. Moisture influences positively on the corrosion of metals, but, when excessive, displaces oxygen and decreases aggression. Soluble salts may increase the aggressiveness of the soil, but when the amount (salt) is excessive, lowers acidity and reduces corrosion. The oxygen content is directly related to moisture and soil texture. If it is compact, very wet or with a higher amount of vegetation, oxygen decreases proportionally [13].

Soil corrosivity is usually estimated or inferred from measurements of resistivity, although this is not quantitative. To assess the aggressiveness of soil with quantitative chemical parameters and electrochemical methods is a critical matter for the prevention, control and evaluation of corrosion of buried structures.

In this research the aggressiveness of soil in the city of Poza Rica on carbon steel, copper, zinc and aluminum was analyzed using electrochemical techniques for evaluating the corrosion rate and the mechanisms that are carried out on metal surfaces.

Experimental methodology

Physical characterization

Based on the technique of mass loss (gravimetric), coupons Fe, Zn and Cu were installed during an exposure period of 40 days. For the morphological study of products of corrosion, an analysis of samples was performed by optical microscopy, and x-ray diffraction.

For soil classification by size, 1 kg sample was placed in a baking dish to let it dry in an oven at a temperature of 80°C for a minimum of 12 hours, then it was stored in a desiccator to cool down and finally passed through a set of sieves to separate particles according to their size. Resistivity measurements against moisture content were performed using the Wenner method. Redox potential measurements were made without changing the sample, an electrode (+) Pt indicator and another reference indicator (-) Cu/CuSO4, connected to a multimeter to record potential difference. This test is important to predict the risk of anaerobic corrosion (especially when the medium contains sulfates). A negative redox potential indicates that the sample is not aerated being very aggressive for the materials. For the determination of pH, 100 g of original sample were dissolved in 100 mL of distilled water and stirred for 5 minutes; the solution was allowed to settle for subsequent decanting and measuring with a potentiometer previously calibrated.

Also, with such solution, the amount of chlorides (Cl^-) present, according to Method 4500-Cl-B-18TH Standard Methods (1992) was determined.

Electrochemical characterization

Usually in Poza Rica, the metal infrastructure that is placed on the soil is at a depth of 40 cm and therefore the sample was collected at the same deep. Samples (working electrodes) carbon steel (Fe), galvanized steel (Zn), copper (Cu) and aluminum (Al), 1x1 in^2 were placed (with prior preparation and surface cleaning), to be evaluated by electrochemical methods 1, 6, 24 hours, with 7 and 17 days of exposure. A potentiostat Field Machine model ACM with 2 channels was used for electrochemical measurements, a cell with electrodes from Cu/CuSO4 as reference and graphite as a counter electrode.

Results and discussion

The results of the physicochemical characterization of soil studied, are shown in Table I, the percentage of moisture; in Table II, the size classification; in Table III, the pH values and chlorides and in Table IV, the measurements of mass loss metals evaluated in control.

According to bibliographic information, the percentage of moisture and characterization of particle size (Table I and II), the floor of the city of Poza Rica is classified as clay and slightly corrosive soils for its resistivity values (Raichev, 2008 Andrade, 1991). The redox potential indicates a trend very susceptible to the risk of anaerobic corrosion (Otero, 2001). The pH and the amount of chlorides present favors the process of corrosion (Table II).

Initial mass (g)	Final mass (g)	Water content (g)	Moisture (%)
1000	839.32	160.68	16.068

Table 1 Percentage of moisture in the soil of Poza Rica.

Particle size (mm)	Mass (g)	Percentage (%)
> 2.38	706	84.11
2.38 a 0.59	85.56	10.20
0.59 a 0.279	10.94	1.30
0.279 a 0.149	5.52	0.66
< 0.149	31.3	3.73
Total	839.32	100

Table 2 Soil granulometry of Poza Rica

Resistivity (Ω/cm^2)	Potencial redox (V)	Cl^- (ppm)	pH
110,000	-0.131	78.658	6.8

Table 3 Number of chlorides, pH and redox potential.

Material	Mass		
	Initial (g)	Final (g)	Difference (g)
Cu	3.5412	3.5176	0.0236
Fe	4.8016	4.7254	0.0762
Zn	4.7371	4.7042	0.0329

Table 4 The measurements of mass loss metals evaluated in control

In Table V the results obtained from the electrochemical methods are shown. The current densities (proportional to the corrosion rate) obtained from the technique Resistance to Linear Polarization are high for carbon steel (in comparison with the other exposed metal), which implies a low resistance to the electron transfer. Aluminum, galvanized steel and copper, however, increase the resistance to charge transfer as time of exposure increases, this means the formation of corrosion products as cuprite for Cu and goethite for Fe.

Identified by X-ray diffraction (figure 6 and 7), forming porous layers on the metal substrate surface decreases corrosion.

	Time	E_{corr} (mV)	RP (Ω/cm^2)	I_{corr} (mA/ cm^2)
Fe	1 h	-706.93	2400.8	1.08E-2
	6 h	-755.67	2405.9	1.08E-2
	24 h	-768.87	2084.3	1.25E-2
	7 d	-786.4	2593.6	1.01E-2
	17 d	-988.75	2141.2	1.22E-2
Zn	1 h	-1114.4	3715	7.02E-3
	6 h	-1012.8	7089.8	3.70E-3
	24 h	-1030.7	8715	3.04E-3
	7 d	-1018.4	20078	1.30E-03
	17 d	-1222.6	5633.8	4.60E-03
Al	1 h	-1279.8	45678	5.70E-04
	6 h	-699.7	186410	1.40E-04
	24 h	-673.76	683390	3.82E-05
	7 d	-757.53	656730	3.97E-05
	17 d	-832.11	3182.2	8.20E-03
Cu	1 h	-164.72	10868	2.40E-03
	6 h	-109.92	17282	1.51E-03
	24 h	-103.66	17282	1.51E-03
	17 d	-213.77	6417	4.06E-03
	17 d	-129.37	11204	2.33E-03

Table 5 Results electrochemical polarization resistance technique in soil of Poza Rica

In Figure 1a, potentiodynamic polarization curves present a mixed control and slow kinetics from the reactions of oxidation and reduction [6]. 1b shows diagrams EIS (Electrochemical Impedance Spectroscopy) in bode for carbon steel, it can be seen in the high frequency region (10^2-10^3 Hz) the formation of corrosion products that increases the resistance as exposure time increases (mainly 24 hours and 7 days of exposure), however, films formed of corrosion products (Fe_2O_3, 2a-2b) are porous by the presence of corrosion by activation in the medium frequency region (1 to 10^2 Hz) that allow diffusion of electroactive species in the visible low frequency region (1 to 10^{-2} Hz).

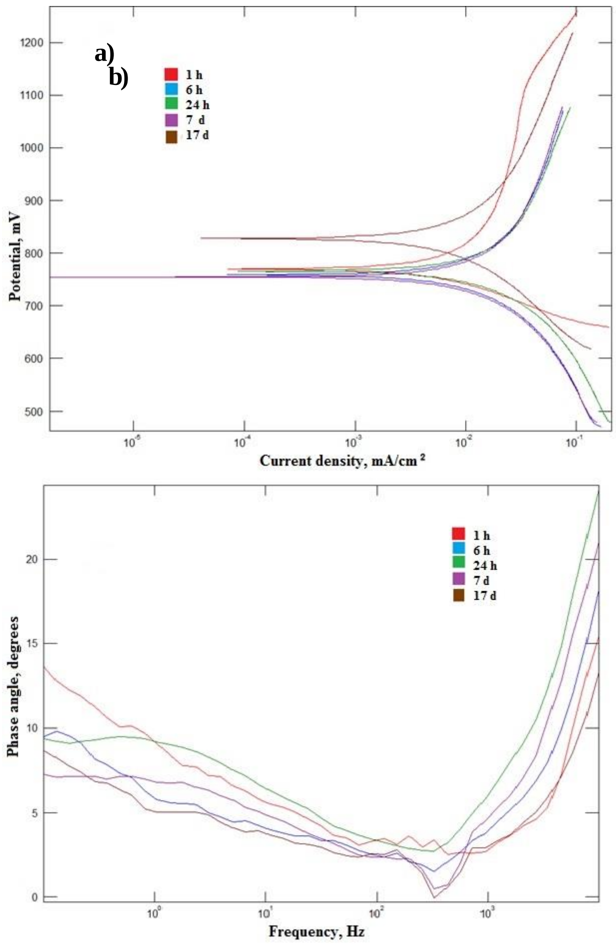


Figure 1 a) Polarization curves and b) impedance diagrams bode for carbon steel (Fe) on soil of Poza Rica at different times of exposure

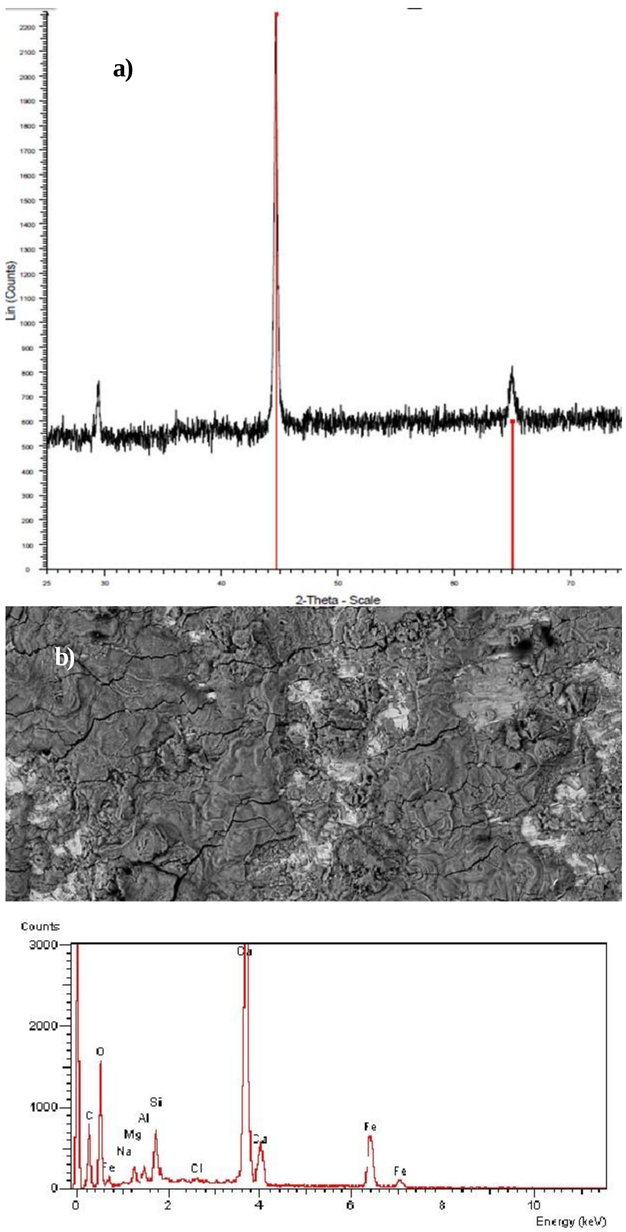


Figure 2 X-ray diffraction and SEM, showing the formation of corrosion products on the surface of Fe, 40 days of exposure on soil of Poza Rica

As shown in figure 3a, potentiodynamic polarization curves obtained for galvanized steel exposed to the aggressive soil in Poza Rica, which showed mixed control. In Figure 3b, EIS diagrams are presented in bode for galvanized steel.

The film of corrosion products (Figure 4a and b) formed by the aggressiveness of the soil (high frequency 10^2-10^3 Hz) increases the strength of the substrate as time of exposure increases (mainly 24 hours, 7 and 14 days of exposure), it being compact and slightly conductive given the RP values (table V). In the mid-frequency region (1 to 10^2 Hz) it can be observed the corrosion by activation in function of days of exposure and limited or semi-infinite diffusion (low frequency (1 to 10^{-2} Hz).

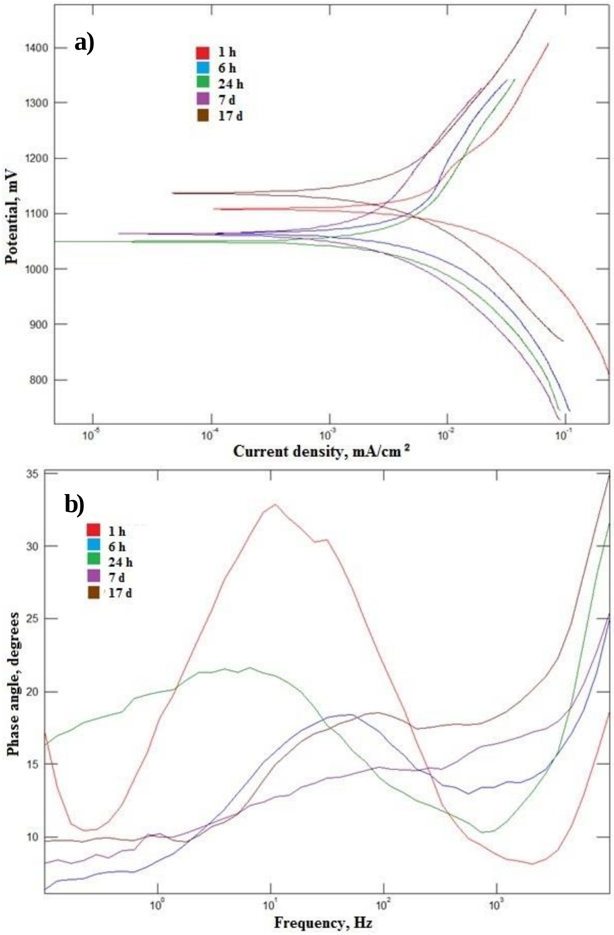


Figure 3 a) Polarization curves and b) impedance diagrams bode for galvanized steel (Zn) on soil of Poza Rica at different times of exposure

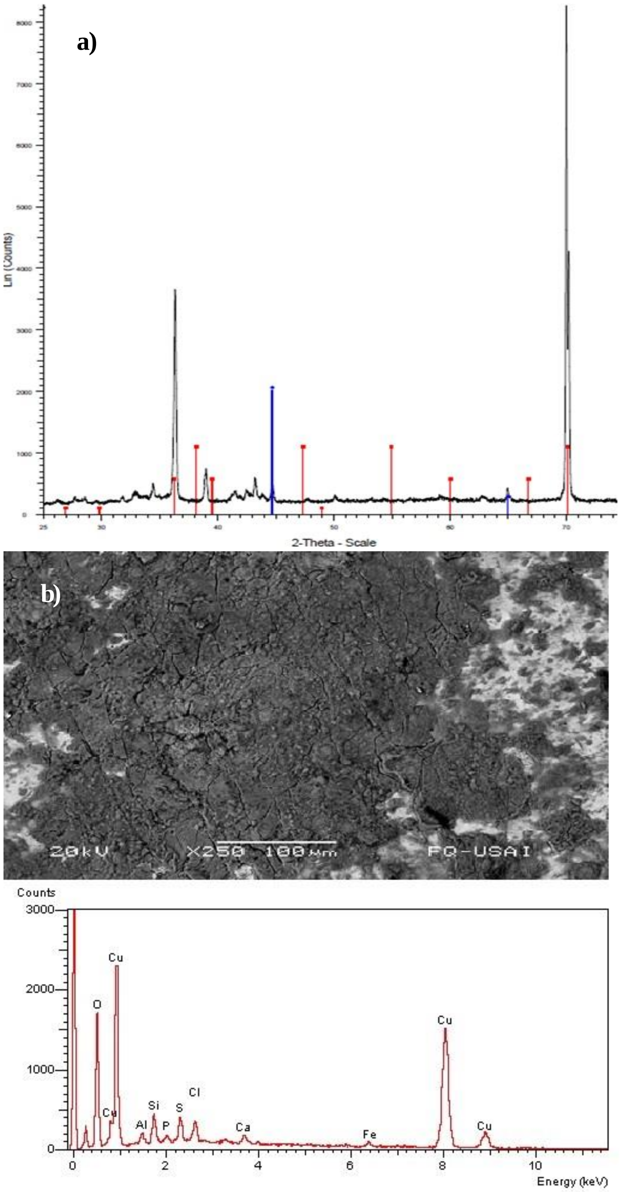


Figure 4 X-ray diffraction and SEM, showing the formation of corrosion products on the surface of Zn, 40 days of exposure on soil of Poza Rica

Potentiodynamic polarization curves obtained for aluminum (Figure 5a) show a mixed control and a decrease in the intensity of current at 24 hours and 7 days of exposure, but increased at 6 hours and 17 days; This can also be confirmed with the values obtained with the PR (Table V) technique.

In Figure 5b diagrams EIS shown in bode for aluminum at different times of exposure in the high frequency region (10^2-10^3 Hz) the formation of compact films of corrosion products increases their resistance the longer the exposure time and a high resistance given to the metal substrate according to strength values obtained with PR technique (table V). In the mid-frequency region (1 to 10^2 Hz) minimal influence of corrosion is observed by activation under 1, 6, 24 hours and 7 days; however, a domain of corrosion is observed by activation at 17 days, which means an increase in the corrosion rate and reduced resistance to electron transfer. In the region of low frequency (1 to 10^{-2} Hz), it is possible to observe a limited diffusion, however, after 24 hours of exposure the process is pure charge transfer and diffusional control known as Warburg impedance [8, 10, 12].

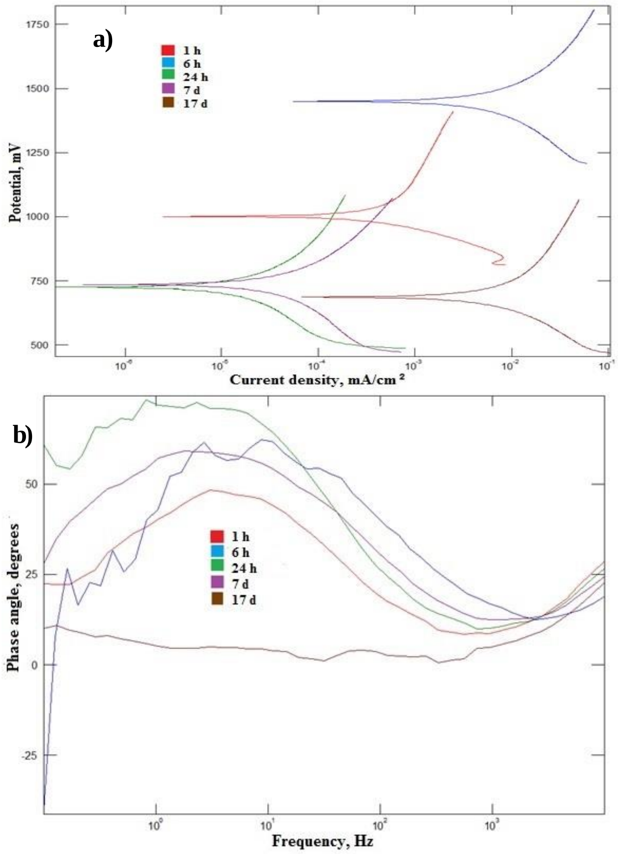


Figure 5 a) Polarization curves and b) impedance diagrams bode for aluminum (Al) on soil of Poza Rica at different times of exposure

The polarization curves (figure 6) show minimum densities of current for the anodic reaction. In figure 6b, behavior of copper shown at different periods of exposure in the high frequency region (10^2-10^3 Hz), the films of products of corrosion formed (Cu_2O identified by XRD, fig.7) increases the resistance substrate by increasing the exposure time. However, in the mid-frequency region (1 to 10^2 Hz) it can be observed an increase in the corrosion process by activation 7 to 17 days with limited diffusion at low frequency. The storm activity, moisture and the oxygen in soil, can influenciate an increased corrosion rate, however, depending on the exposure time, copper forms passive films that can protect from aggressive soil [3, 5, 7 and 11].

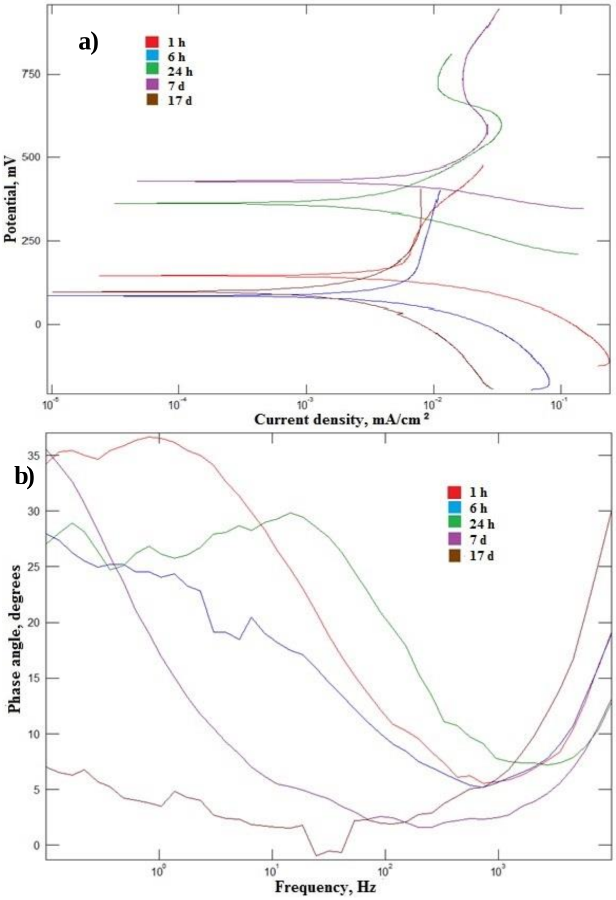
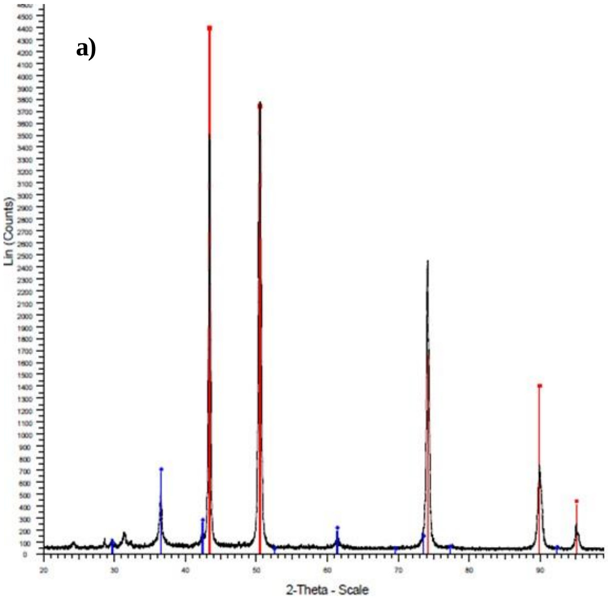


Figure 6 a) Polarization curves and b) impedance diagrams bode for copper (Cu) on soil of Poza Rica at different times of exposure



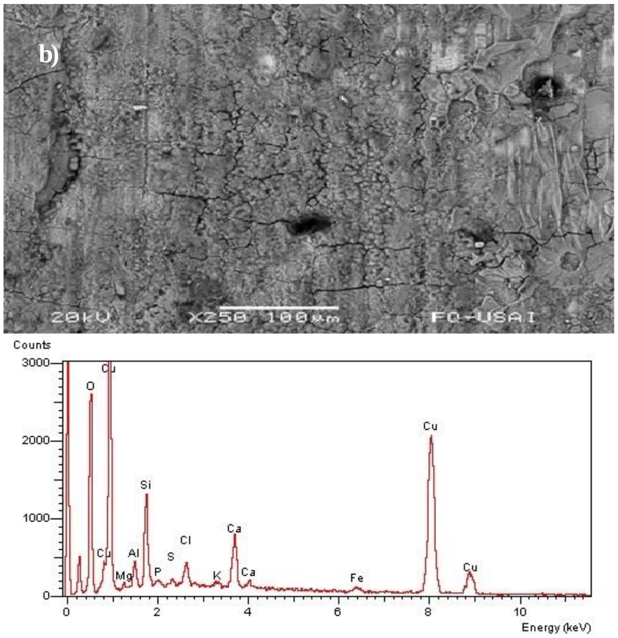


Figure 7 X-ray diffraction and SEM, showing the formation of corrosion products on the surface of Cu, 40 days of exposure on soil of Poza Rica

Conclusions

The presence of ions in the studied soil increases its conductivity and decreases its resistivity favoring the corrosive behaviour by the formation of differential aeration cells.

Copper and galvanized steel are metals that showed an improved corrosion resistance because of the minimum amount of missing mass.

According to the results obtained with electrochemical techniques form the carbon steel corrosion products which form a porous film incapable of reducing the corrotion by activation due to environmental conditions and characteristic of the material.

However, for materials such as Cu, Al, and galvanized steel (Zn) corrosion products (identified by XRD) are very compact protective films, such as patina or alumina, manage to seal the surface of the substrate by decreasing the corrosion rate as time of exposure increases.

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