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Influence of Ultraviolet Light Irradiation on the Corrosion Behavior of Carbon Steel AISI 1015

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Corrosion of carbon steel in sodium chloride solution was studied under ultraviolet illumination using weight loss, polarization, electrochemical impedance spectroscopy and current transient tests. The polarization test revealed an increase in the corrosion current density observed under UV illumination. The impedance spectroscopy indicated that the charge transfer resistance of the system was decreased by irradiation of UV light on a carbon steel electrode. The weight loss of carbon steel in solution increased under UV light, which confirms the results obtained from electrochemical measurements. We propose that the main effect of UV irradiation is on the oxide film, which forms on the surface. Thus, in presence of UV, the conductivity of oxide film might increase and lead to higher metal dissolution and corrosion rate.

Key words: corrosion, surface, electrochemistry, scanning electron microscopy

1. INTRODUCTION

Corrosion behaviors of carbon steels used in seawater environments are strongly affected by factors such as humidity, temperature, pollutants, aggressive ions, pH of seawater, and wet and dry cycles. Recently, the effects of sunlight and ultraviolet (UV) light on the corrosion of metals have attracted considerable attention [1-7]. It has been reported that the weight loss of some metals like pure zinc and zinc alloy immersed in fresh water is higher in UV light than in the dark conditions [1,2] and other metals like 304 stainless steel and aluminum are inhibited from localized corrosion by the irradiation of UV light [3,4]. These effects are due to covered semiconductive materials such as iron oxides and passive films which usually form on the surface of these metals [8,9]. The action of light in changing the electric current flowing through a metal and the potential difference between illuminated and dark electrodes is a well-known phenomenon [10].

Carbon steels without any coating have been developed for maintenance-free structures and offshore pipelines, because the rust formed on the steel surface itself prevents the progress of corrosion. Although shallow depth steel structures and pipelines in seawater are subjected to strong solar light, the effect of UV radiation on corrosion and the rust formation behavior on carbon steel is not well known. The purpose of the present paper is to investigate the effect of UV irradiation on the corrosion rate and corrosion behavior of carbon steel by polarization and impedance spectroscopy.

2. MATERIALS AND METHODS

A carbon steel AISI 1015 electrode (C: 0.16 wt%, Si: 0.32 wt%, Mn: 0.35 wt%, P: 0.03 wt%, S: 0.02 wt%, Fe: Bal.) was used as a working electrode. Samples for electrochemical experiments were cut from a cylindrical rod with a cutter machine. Each sample was covered with lacquer and then sealed by polyester resin so the exposed surface area of each electrode was equal to 0.81 cm^2. For weight loss measurement, cubic samples were cut from the same carbon steel with an exposed area of 6.26 cm^2. The exposed areas of the electrodes were mechanically abraded with 220, 400, 600, 800, 1000 and 1200 grades of emery paper, degreased with acetone and rinsed with distilled water before each electrochemical experiment.

Corrosion tests were carried out in a 3.5 wt% NaCl aqueous solution in the dark, laboratory light and under UV light irradiation (peak wave length: λ=365 nm) at room temperature. UV light irradiated the solution and the electrode surface directly. To check the validity of the results obtained from the electrochemical tests, weight loss measurements were undertaken in the three conditions, sunlight radiation, shadow and dark, and for each of them, two specimens were used for a period of seven days. In the polarization tests, the depth of the specimen in solution was kept at about 15 mm and the solutions were open to the air. In the weight loss measurement, this depth was about 7 cm but the volume of the solu-

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tion was kept at 1 L. After the test was finished, the specimens were taken out of the beaker, rinsed with distilled water and dried in a vacuum chamber. The rust was then removed completely from the surface of the specimens by hand washing. After the specimens were cleaned with the ultrasonic cleaner in 10% diammonium hydrogen citrate to dissolve all the remaining rust, the surface was rinsed in distilled water and finally the weight of specimens when completely dry were measured to obtain the weight loss. The surface morphology of the electrode was evaluated by scanning electron microscopy (VEGA\\TESCAN).

The apparatus for electrochemical investigations consisted of a computer controlled AutoLab potentiostat/galvanostat (PGSTAT 302N) potentiostat corrosion measurement system at a scan rate of 1 mV/sec. Electrochemical measurements were carried out in a conventional three-electrode glass cell. A platinum electrode was used as a counter electrode and a saturated calomel electrode as the reference electrode. Polarization experiments were done in a beaker containing 200 ml of 3.5 wt% NaCl solution at a temperature of 25±1 °C. Experiments were carried out from −1200 mV to −100 mV with respect to the reference electrode.

Signals in electrochemical impedance spectroscopy (EIS) measurements were applied in a frequency range of 100 kHz to 10 mHz with a peak-to-peak A.C. amplitude of 10 mV. The impedance diagrams were plotted in the Nyquist representation. In all EIS measurements and polarization experiments, before recording, the working electrode was maintained at its open circuit potential for 20-25 minutes until a steady state was obtained.

Fitting of experimental impedance spectroscopy data to the proposed equivalent circuit was done by means of home-written least square software based on the Marquardt method for the optimization of functions and Macdonald weighting for the real and imaginary parts of the impedance [11,12].

3. RESULTS AND DISCUSSION

3.1. Weight loss measurement

Weight loss measurements were undertaken in three conditions, sunlight radiation, shadow and dark, and for each of them two specimens were used for a period of seven days. Table 1 shows the weight loss obtained for the two samples in each condition. It is evident from these results that the corrosion rate of carbon steel at the condition of sunlight radiation is 3.5 times higher than that of shadow and dark, and that means that in a similar solution only sunlight irradiation on the metal and solution will increase the rate of corrosion.

3.2. Corrosion behavior of carbon steel under UV illumination

Potentiodynamic anodic and corresponding cathodic polarization curves with and without UV illumination are shown in Figure 1. In all conditions the anodic polarization curves demonstrated that the carbon steel was in an active state, without any indication of an active-passive transition. The polarization curves showed Tafel type behavior in these samples. The Tafel calculations are listed in Table 2, where E_{corr}, I_{corr}, CR, β_a, β_c and R_p are the corrosion potential, corrosion current density, corrosion rate, anode Tafel constant, cathode Tafel constant and polarization resistance, respectively. Temperature was checked during the experiment and was constant at about 25±1 °C.

These Tafel polarization diagrams illustrate that the corrosion rate of carbon steel in the presence of UV light which irradiated both the surface and the solution is greater than that of carbon steel where laboratory light conditions are used. Since all the other parameters, pH, temperature and solution concentration, in all the cases were the same, we conclude that the irradiation of high energy light, e.g., UV light on the surface of carbon steel and the bulk of solution, causes a higher corrosion rate in carbon steel in this solution. These results are very compatible with and verify the results obtained from weight loss measurements as discussed before.

Figure 2 shows metalographs of the surface of the carbon steel electrodes that were cleaned after polarization (Fig. 1)

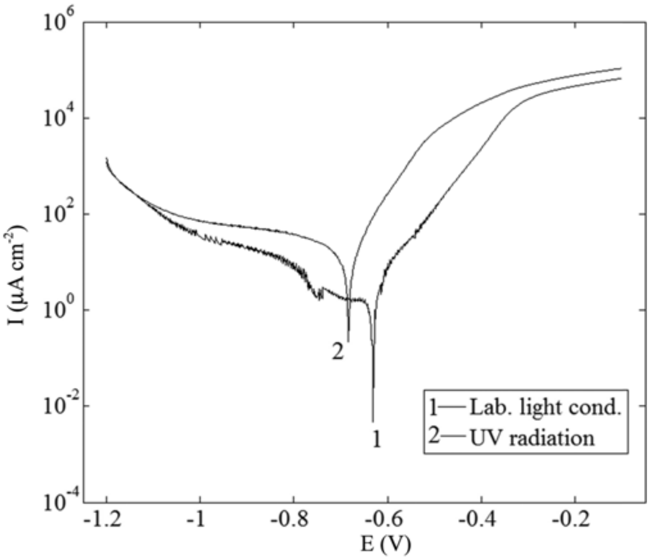

Fig. 1. Polarization curves of carbon steel electrodes immerced in NaCl 3.5 wt% under laboratory and UV light conditions.

Table 1. Weight loss and corrosion rates of six carbon steel electrodes immersed in NaCl 3.5 wt% obtained by weight loss measurements

	Sunlight #1	Sunlight #2	Shadow #1	Shadow #2	Dark #1	Dark #2
Weight loss(mg)	29.7	29.2	14.9	13.4	9.9	9.4
Corrosion rate (mpy)	12.59	12.38	6.32	5.68	4.20	3.20

Table 2. Polarization parameters in the corrosion of carbon steel electrode immersed in NaCl 3.5 wt% solution

	$-\beta_c$ (mV/dec)	β_a (mV/dec)	E_{corr} (mV)	I_{corr} (μA)	CR (mpy)	R_p (Ω)
UV radiation	854	68.4	−666	22.7	12.78	1211
Lab. light cond.	331	80.5	−632	2.46	1.38	11287

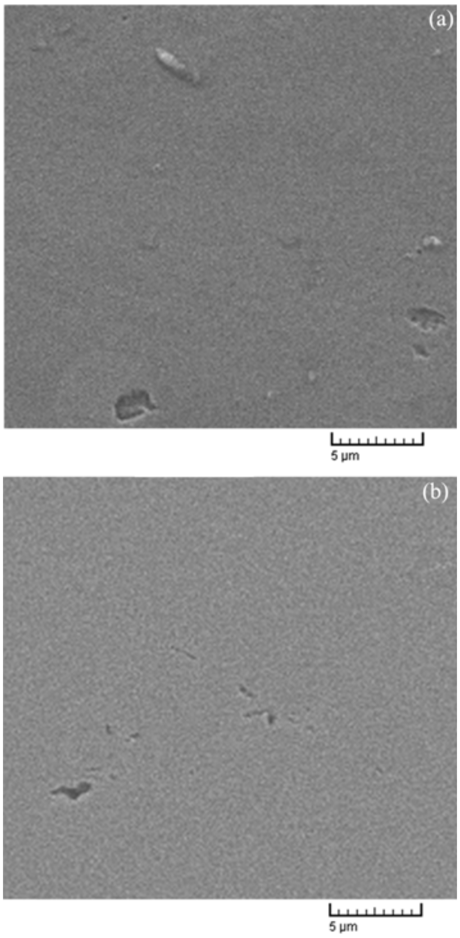

Fig. 2. SEM image of carbon steel electrodes that were cleaned after constant current polarization in (a) UV and (b) laboratory light conditions.

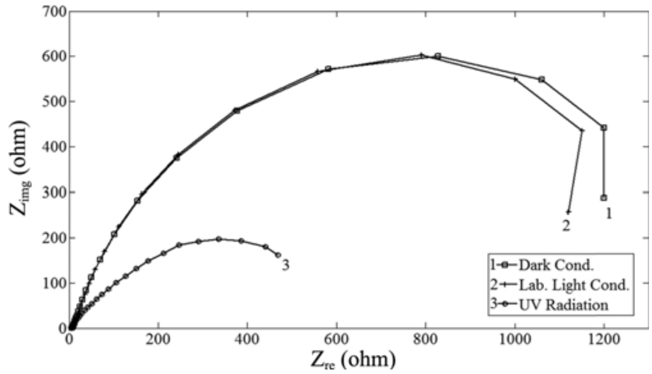

Fig. 3. Nyquist plots of carbon steel electrodes immersed in 3.5 wt% NaCl under dark, laboratory and UV light conditions.

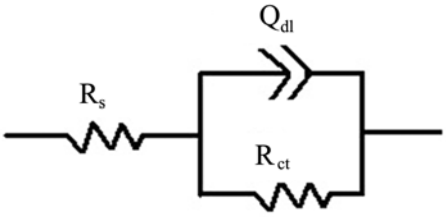

Fig. 4. The equivalentcircuit model used for impedance spectra obtained for carbon steel in a 3.5 wt% solution.

Table 3. Equivalent circuit parameters in the corrosion of steel electrode in 3.5 wt% NaCl solution

	R_{ct} (Ω)	Q_{dl} (F)	n	R_s (Ω)	D_s
UV radiation	651	0.018	0.68	4.5	2.47
Lab. Light cond.	1475	0.004	0.83	5.9	1.2
Dark cond.	1515	0.006	0.85	6.5	1.17

in UV and laboratory light conditions. It is clear that the environment with UV light irradiation is more aggressive and more corrossive and the metal loss is greater.

The indications given by the polarization curves were complemented by impedance measurements made at the OCP in three different environments. The Nyquist plot for the steel sample in a 3.5 wt% NaCl aqueous solution at OCP is shown in Fig. 3. The data reveal that the impedance diagram with a one-time constant consists of a capacitive loop due to charge transfer resistance and double layer capacitance. The impedance spectra were analyzed by fitting the experimental data to the Randle equilavalent circuit model [13-15], as shown in Fig. 4. Table 3 illastrates the equivalent circuit parameters for impedance spectra obtained in Fig. 3. The simplest approach requires the theoretical transfer function $Z(\omega)$ to be represented by a parallel combination of a resistance R_{ct} and a capacitance C, both in series with another resistance R_s.

$$Z(\omega) = R_s + \frac{1}{1/R_{ct} + i\omega C} \tag{1}$$

where ω is the frequency inrad/s, $\omega = 2\pi f$ and f is frequency in Hz.

To obtain a satisfactory impedance simulation of steel, it is necessary to replace the capacitor (C) with a constant phase element (CPE) Q in the equivalent circuit. The most widely accepted explanation for the presence of CPE behavior and depressed semicircles on solid electrodes is microscopic roughness, which causes an inhomogeneous distribution in the solution resistance as well as in the double-layer capacitance [16].

The constant phase elements CPE_{dl}, R_s and R_{ct} correspond to the double layer capacitance, solution resistance, and charge transfer resistance, respectively. This electrochemical circuit fit acceptably on the EIS spectra with a mean square error of less than 0.05 ($x^2 < 0.05$).

The Nyquist plots in Figure 3 obviously confirm the potentiodynamic polarization results. They confirm that the charge transfer resistance, R_{ct}, decreases significantly in the presence of UV light radiation compared to the dark and shadow environments. These data indicate a modification in the electrical properties of the charge transfer region by a UV light presence. The resistances of the solution decreased with irradiation of UV light but this decrease was not significant, which means that the main effect of UV light is on the charge transfer reaction which can be due to more conductivity of the corrosion product [17,18] under UV illumination. But this effect is less in the bulk of solution.

The value of fractal dimension (Ds) can be obtained using the average of n values signifying deviation [19] from the pure capacitance of a CPE in impedance measurements at different offset potentials according to the following equation [20]:

$$D_s = \frac{1}{n} + 1 \tag{2}$$

where n is the frequency independent parameter, $Q=C(jw)^n$. The fractal dimension of the surface, D_s, can take values between 2, for an ideally flat surface, and values less than 3 for rough surfaces. The system under UV illumination has a higher fractal dimension. Thus, the surface was damaged and the corrosion was higher, which is in agreement with Fig. 2.

Figure 5 shows the Tafel polarization curves of carbon steel irradiated with UV light, but with different times of exposure. It is evident that the specimen that was irradiated more than another had a higher corrosion current density. The kinetic parameters of potentiodynamic polarization are shown in Table 4.

To investigate whether the effect of UV light on the corrosion rate is because of irradiation on the surface of the carbon steel or on the bulk of the solution, UV light was irradiated from behind the specimen in such a way that the surface of the electrode was not irradiated directly. Figure 6 indicates the polarization curves of carbon steel in direct irradiation and back irradiation of UV light, and corresponding polarization data were observed in Table 5. It can be observed that in the case of back irradiation, the current density was lower than the direct UV light. Therefore, the effect of UV light on the corrosion rate of carbon steel is due to both effects on the surface of carbon steel and the bulk of solution.

Figure 7 shows the impedance spectra obtained from back irradiation, direct UV irradiation and dark conditions. Relative equivalent circuit parameters of impedance spectra are listed in Table 6. As it can be seen in Fig. 7 and Table 6, the charge transfer resistance in the case of back irradiation of UV light is higher than that in dark conditions and lower than

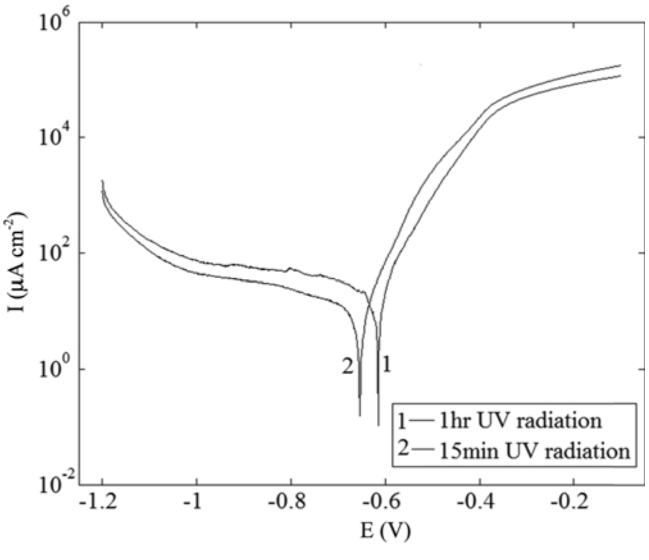

Fig. 5. Polarization curves of carbon steel electrodes immersed in a NaCl 3.5 wt% solution in two different exposure times of UV light irradiation.

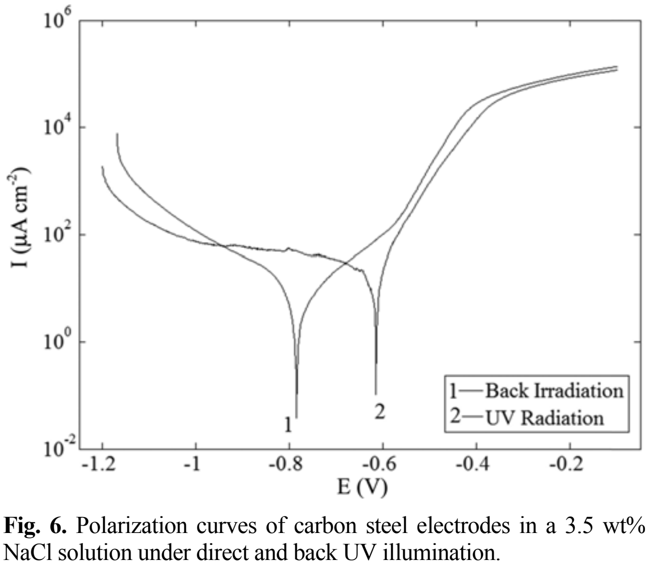

Fig. 6. Polarization curves of carbon steel electrodes in a 3.5 wt% NaCl solution under direct and back UV illumination.

Table 4. Polarization parameters in the corrosion of carbon steel electrode immersed in NaCl 3.5 wt% solution: the effecte of time of UV illumination

	$-\beta_c$ (mV/dec)	β_a (mV/dec)	E_{corr} (mV)	I_{corr} (μA)	CR (mpy)	R_p (Ω)
1 h Radiation	1230	79	–613.1	27.3	15.36	1180
15 min Radiation	929	58.3	–635.6	14.4	8.10	1654

Table 5. Polarization parameters in the corrosion of carbon steel electrode immersed in NaCl 3.5 wt% solution: direct and back illumination

	$-\beta_c$ (mV/dec)	β_a (mV/dec)	E_{corr} (mV)	I_{corr} (μA)	CR (mpy)	R_p (Ω)
UV radiation	854	68.4	−666	22.7	12.78	1211
Back irradiation	150	238	−785	7.68	4.32	5202

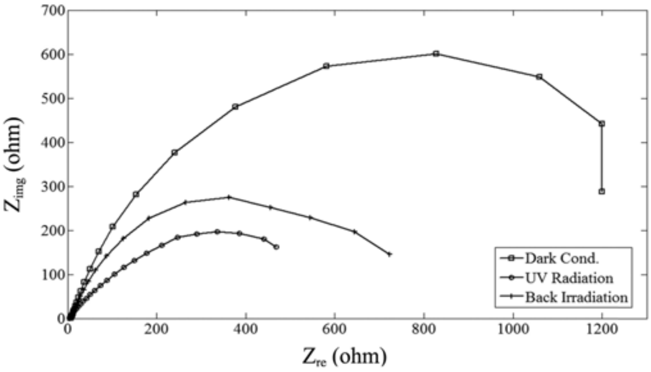

Fig. 7. Nyquist plots of carbon steel electrodes immersed in 3.5 wt% NaCl solution in dark conditions and under direct and back UV illumination.

Table 6. Equivalent circuit parameters in the corrosion of steel electrode in 3.5 wt% NaCl solution: direct and back illumination

	R_{ct} (Ω)	Q_{dl} (F)	n	R_s (Ω)
UV radiation	651	0.018	0.68	4.5
Back irradiation	788	0.01	0.77	5
Dark cond.	1515	0.006	0.85	6.5

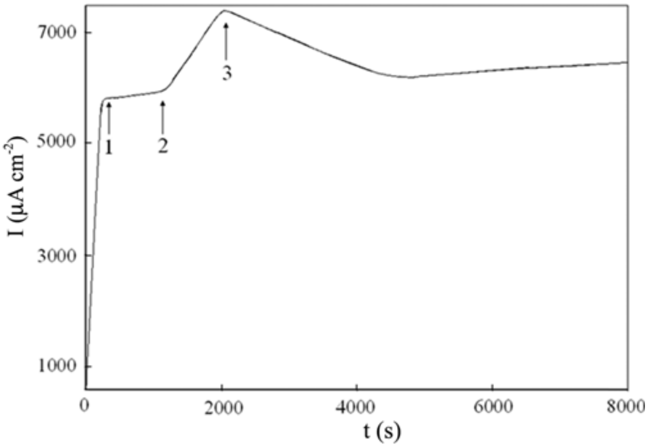

Fig. 8. Effect of UV light on the current transient of a carbon steel electrode immersed in 3.5 wt% NaCl solution. From left to right: 1) first arrow shows the time of steady state, 2) second arrow shows the time at which the UV lamp was turned on. 3) third arrow shows the time of the second steady state and the time at which the UV lamp was turned off.

that in direct irradiation of UV light. These results indicate that the effect of UV light is more significant on the surface of carbon steel, specially the oxide film layer.

3.3. Current transient under UV illumination

The current transient method was used to determine the anodic current of carbon steel in the presence and absence of UV light at a specific anodic potential. The plot of current versus time at a potential of -450 mV vs. a saturated calomel reference electrode is shown in Fig. 8. The UV lamp was off from the beginning of the test, and the current normally increased as a result of metal dissolution to reach a steady state constant value of about 5750 μA at 350 seconds after starting the test. We concluded that a layer of corrosion products formed on the surface of the carbon steel electrode and prevented the current from increasing and held the current at a constant value. In the 1000th second, the UV lamp was turned on and irradiated the surface of the carbon steel electrode and the bulk solution. The anodic current density and corrosion rate obviously increased again and reached another constant value of 7600 μA at about the 2000th second. The UV lamp was turned off again after some minutes and as we expected the anodic current density approached the value without illumination with the lower slope. This lower current transient slope was ascribed to the memory effect by Kozlowski *et al.* [21] in which the UV light irradiation causes an irreversible change of the oxide film on the metal surface in an aqueous solution. This figure clearly illustrates the effect of UV light irradiation on the corrosion current and corrosion rate of the carbon steel electrode as well. It is evident that the current will become higher in the presence of UV light and it will decrease by removing the UV light.

3.4. Impedance spectroscopy in seven consecutive days

The EIS measurements were undertaken over seven consecutive days in three different field conditions. Three carbon steel electrodes were immersed in a NaCl 3.5 wt% solution and each of them was placed in different conditions: dark, shadow and sunlight radiation. After each 24 h, the EIS tests from each cell were done separately in light laboratory conditions. Figure 9 shows the impedance spectra of these three environments from first day to seventh day and the impedance parameters values of R_s, R_{ct} and CPE_{dl} of carbon steel with respect to equivalent circuit model (Fig. 4), are summarized in Table 7.

It is evident that throughout all the days the charge transfer resistance of sample in sunlight was significantly lower than the dark and shadow conditions. This confirms the results obtained under the UV lamp in the laboratory. In sunlight, the steel was corroded severely and its surface was more active for a further corrosion process. Therefore the effect of UV in the sunlight wavelength is the main cause of this decrease in charge transfer resistance and increase in corro-

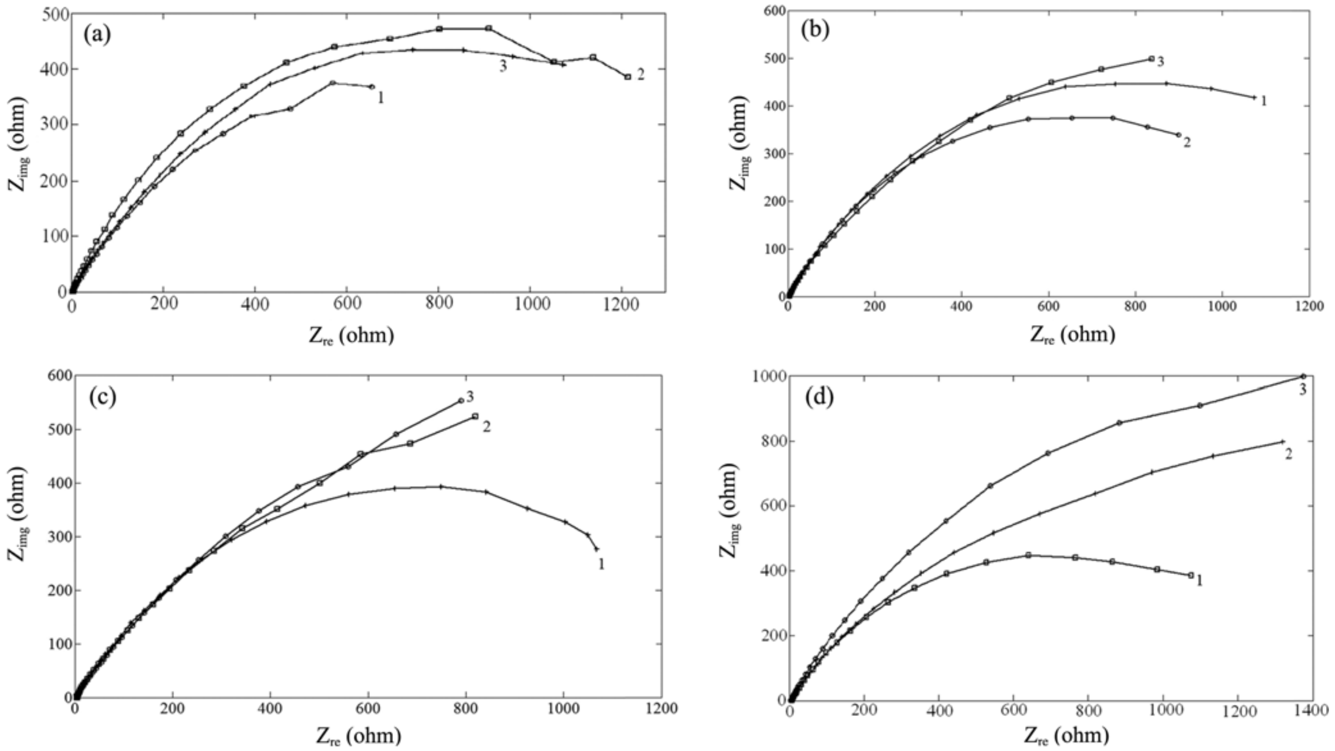

Fig. 9. Nyquist plots of carbon steel electrodes immersed in 3.5 wt% NaCl solution remain in different conditions (1) sun light, (2) shadow and (3) dark. Experiments were done in labolatory light conditions and different days (a) 1st, (b) 2nd, (c) 4th and (d) 7th day.

Table 7. Polarization parameters in the corrosion of carbon steel electrode immersed in NaCl 3.5 wt% solution: effect of time of sunlight irradiation

	R_1 (Ω)	Q_1 (F)	n	R_s (Ω)
1st Sunlight	1244	0.018	0.6	4.5
1st Shadow	1594	0.007	0.7	4
1st Dark	1613	0.008	0.64	3.9
2nd Sunlight	1286	0.013	0.62	1.2
2nd Shadow	1639	0.01	0.65	3.5
2nd Dark	1720	0.016	0.68	3.6
4th Sunlight	1357	0.006	0.61	2.8
4th Shadow	1878	0.017	0.65	4.5
4th Dark	1932	0.016	0.65	5.5
7th Sunlight	1520	0.009	0.65	5.3
7th Shadow	2715	0.009	0.67	6.2
7th Dark	2834	0.012	0.75	6.5

sion current.

In these results as listed in Table 7 one which is interesting is the increasing charge transfer resistance of each environment after each day. We concluded that the corrosion products layer formed on electrode surface were thicker and therefore inhibited corrosion [22].

3.5. Mechanism of Photo-corrosion

It was evident that by irradiation of sunlight or UV light on the surface of carbon steel and the bulk of solution, both the resistance of the solution (R_s) and the resistance of the charge transfer (R_{ct}) decreased. According to back irradiation data, UV effect is more significant for illumination on the electrode surface and charge transfer resistance. This means that the essential effect of UV irradiation is on the oxide film, iron oxide, which forms on the surface and some modification of the properties of the solution. Therefore, by UV light energy, the conductivity of oxide film might be increased. The metal iron oxide is a semi-conductor, and some reaction will proceed in the presence of high energy photons like UV light [6,8-9,23-24].

In semi-conductor materials there is not only a valence band in an atom but also it is a conduction band above the valence band with different energy equal to E_g which is called band gap energy. If photons with energy greater than E_g irradiate on the valence band electron, this electron migrates to the conduction band so that hole (h^+) is produced in the valence band.

The irradiation induces an increase of donor density. When the oxide film under positive bias is irradiated by UV light with energy higher than the band-gap energy of the oxide, electron-hole pairs are generated in the oxide. Appreciable numbers of the excited electrons and holes recombine with each other in the oxide film and at the oxide surface. Some of the electrons excited in the conduction band migrate to the oxide/metal substrate interface and holes in the valence band to the oxide/solution interface.

$$h\upsilon \rightarrow h^+ \text{ (valence band)} + e^- \text{ (conduction band)} \quad (3)$$

The holes at the oxide surface decompose water to the oxygen molecule and protons.

$$2H_2O + 4h^+ \rightarrow O_2 + 4H^+ \quad (4)$$

However, not all holes at the oxide surface react with water and the remaining part of the holes accumulates at the oxide surface. The accumulation of holes at the surface may induce a decrease in the potential drop in the layer. When the oxide electrode is controlled potentiostatically, the decrease of the potential drop at the space charge layer in the oxide results in an increase of the potential difference at the oxide/solution interface. Since the cationic charge transfer rate at the oxide/ solution interface is a function of the potential difference at the interface. Therefore, the transfer rate of metal ions from the oxide film to the solution is accelerated by the UV light irradiation due to the increase of the interfacial potential difference. On the other hand, the effect is a weakening of the metal-O bond in the oxide. The holes accumulated in the oxide film may react with the -O bond, breaking the bond to form oxygen vacancies [6].

Positive holes in the valence bands play a role in some reactions and produce advanced oxygen processes (AOPs) that contain very active oxygen species like OH· (hydroxyl radical), $O{\cdot}_2^-$, O^- (super oxide radical anion), $HO{\cdot}_2$ (perhydroxyl radical) [7,25,26]. These active oxygen species promote the formation of rust at the surface of carbon steel, which means the increasing corrosion rates in the surface of carbon steel by reduction of active oxygen which are super oxidant agents [6,7,25]. These AOPs at the surface of carbon steel increase the current density of the charge transfer and therefore decrease the resistance of the charge transfer. This system is based on the generation of very reactive oxidizing free radicals such as OH·, $O{\cdot}_2^-$, and O^-.

By measuring the oxygen concentration in the solution in presence and absence of UV light, it was observed that by irradiation of UV light on the solution the oxygen concentration decreased from 8.974 ppm to 7.913 ppm and after turning off the UV lamp, and the oxygen concentration increased again to 8.492 ppm. This confirms that the oxygen content of the solution converts to an active oxygen radical and by removing the UV light, these radicals recombine again and generate an oxygen molecule ($O_2 + e^- \rightarrow O{\cdot}_2^-$).

4. CONCLUSION

The corrosion behavior of carbon steel under three conditions, UV light irradiation, laboratory light and dark conditions, was investigated by electrochemical experiments using 3.5 wt% NaCl solutions. Weight loss measurements were also carried out in the three conditions, sunlight, shadow and dark conditions using the same solution. In polarization tests, an increase in the anodic current density and the corrosion rate of carbon steel appeared under UV light. Since iron oxides exhibit a semiconductor-like behavior, the current density increases by the migration of photoelectrons and production of holes at the interface. EIS tests confirmed that in the presence of UV light the charge transfer resistance of the system decreases significantly, which is in agreement with polarization data. The immersion test indicated that the sunlight increased the weight loss of the specimens within seven days. This is explained by the promotion of corrosion and rust formation due to the active oxygen generated by photoelectrochemical reactions under UV light.

The photo-corrosion is induced by an accumulation of photo-excited holes at the oxide surface, probably because the accumulation may increase the interfacial potential difference at the oxide surface and weaken the M-O bond of the oxide. Therefore, the effect is due to photo-enhanced electromigration of charged defects like oxygen vacancies and interstitial Fe in the oxide film.

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