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Corrosion behavior of different stainless steel alloys exposed to flowing fresh seawater by electrochemical impedance spectroscopy (EIS)

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ABSTRACT

EIS technique was used to study the effect of the seasonal changes of the Arabian Gulf seawater on the corrosion behavior of UNS No. S 30400 stainless steel, UNS No. S 31600 stainless steel and UNS No. S 62800 sanicro 28 that were exposed to continuous fresh seawater for 180 days. Two types of additives (4 ppm of Cl_2 and 5 ppm of NH_3) were also added to the seawater to investigate the effect of residual seawater pollutants on the surfaces of these alloys. At the end of the tests, visual inspection revealed a thin layer of marine micro fouling was spread on the whole surface of the alloys, whereas the corrosion parameters obtained by EIS technique showed a slight increase in the corrosion resistance of the tested alloy, with the decrease of the seawater temperature. In addition, the corrosion resistance was increased for SS 304 and SS316, when 4 ppm of chlorine was added to the seawater, however there was insignificant influence of the ammonia addition to seawater, observed on the tested samples.

Keywords: Stainless steel alloys; Seawater corrosion; EIS; Marine fouling

1. Introduction

Stainless steels are widely used today as construction materials in aggressive media such as seawater media due to their good corrosion resistance. For instance, process equipments in desalination and oil production plants which employ the Arabian Gulf seawater as a coolant, are usually made of stainless steel alloys including condensers, heat exchangers, pumps and evaporators. It is known that the seasonal changes of the Arabian Gulf seawater ,which was used in this study, increase the salinity of the seawater in the summer months due to evaporation factor because of the severe hot weather, and decreases the salinity in winter months due to the rain and to the low rate of seawater evaporation. As a result, Cl^-, SO_4^{2-} and F^- ion concentrations were found to increase in the summer months, and decrease in the winter months in the seawater [1,2]. Furthermore, the changes in the seawater temperature due to the seasonal changes are known to influence the growth and the activity of the micro organisms such as bacteria, algae, and fungi. Marine microorganisms are associated with a phenomenon widely known as marine fouling which is defined as a community of organisms found growing on permanently submerged surfaces of objects in seawater. The growth of this community usually interferes with the efficient use of the surfaces. For example, the growth of such community, even up to a few micrometers thick, has been shown to have effects on the flow reduction of the fluids through the pipelines, reduction of heat transfer in the heat exchangers systems, reduction in the ship speed and encrusting of support legs of oil rigs, causing what is known as microbiologically induced corrosion (MIC). Different types of bacteria cause corrosion by various mechanisms ranging from formation of differential aeration cells to production of aggressive environments through chemical changes [3–5].The formation of aerobic microorganisms colonizes on the surface of some stainless steel alloys has been reported to shift the open circuit potential (OCP) in the noble direction. This phenomena is known as the ennoblement of stainless steel and usually observed in fresh water and seawater. The effect of the colonization increases the OCP to the value of +350 mV versus the saturated calomel electrode (SCE).The problem of the stainless steel ennoblement is by increasing the E_{corr} to the value above the metal pitting potential, and as a result the risk of localized corrosion initiation and propagation will increase [6,7]. Furthermore, failures of the stainless steel equipments employed in desalination and oil production plants are often reported and attributed to the effect of the residual pollutants found in the seawater such as chlorine and ammonia. For biofouling control, 0.2–0.5 ppm of chlorine is added to seawater to prevent marine growth, while residual ammonia is also found in seawater discharge next to petrochemical plants utilizing seawater as a cooling medium. Thus, it becomes important to investigate the effect of the seasonal changes on the Arabian Gulf seawater as a coolant, on the corrosion's characteristics of materials, which commonly used in desalination plants, by conducting electrochemical impedance tests for stainless steel alloys, under dynamic condition for 180 days of exposure. The EIS technique was used in this study, which is a powerful in situ technique to investigate the corrosion behavior of the alloys, such as the polarization resistance and the double layer capacitance of the surface of the sample, and the solution resistance, without deterioration of the marine formation buildup on the surface of the examined samples. Impedance spectra, in the forms of Nyquist, plots were generated during the tests. EIS calculations were based on a simple electrochemical cell for uncoated specimen (Randles model), thus R_p and R_{sol} values were measured by taking the tangential lines at the lowest and highest frequencies of Bode plot and extending two lines from those values to the ordinate (z-axis) [8].Then at the intersection the lowest frequency with the z-axis, the $R_p + R_{sol}$ will be determined. In the mean time, the intersection of the line of the highest frequency with the z-axis, the R_{sol} will be determined. Therefore, the subtraction of the ($Rp + R_{sol}$) from R_{sol} will yield the Rp, whereas the double layer capacitance (C_{dl}) is calculated at low frequency based on the extrapolation of the intersection line at frequency equal to 0.16 Hz from the x-coordinate, to the y-coordinate [8]. The current density I_{corr}, can be calculated from the following equation [8]:

$$R_p = \beta_a \cdot \beta_c / 2.303 \cdot I_{corr} \left(\beta_a + \beta_c\right) \quad (1)$$

where R_p (KΩ.cm^2) is the polarization resistance obtained from the Bode plot, β_a and β_c are the Tafel coefficients, assumed equal to 120 mV/dec. Tafel coefficients were assumed to be equal to 120 mV/dec because of the difficulties of obtaining Tafel coefficients under the dynamic conditions. It is worth mentioning that the estimated corrosion density was accomplished by assuming a proportionality constant of $B = 0.025$ V between the obtained polarization resistance and the corrosion current. Furthermore, the corrosion rate of the alloys was calculated by Faraday's law, as an expression of the corrosion penetration rate [9], which is:

$$\text{Corrosion penetration rate (mpy)} = K\left(aI / n\rho\right) \quad (2)$$

where a is the atomic weight of the alloy, I is the current density in A/cm^2, n is the number of electron lost, ρ is the density in g/cm^3, K is a constant equal to 0.129.

2. Experimental

Metallic samples of three stainless steels were used in this study. Stainless steels were UNS No. 304 (19% Cr, 9% Ni, 0.45% Mn, and balance of Fe), UNS No. 316 (18% Cr, 12% Ni, 2.5% Mo, 2% Mn, and balance of Fe), and sanicro 28 (27% Cr, 31% Ni, 3.5% Mo, 2% Mn, 1% Cu, 0.002% C, and balance of Fe). All the samples were fabricated in circular form with dimensions of 2 cm in diameter and 0.15 cm in thickness for both open circuit potential measurement and EIS tests. Then all samples were grinded by silicon carbide papers until the finest grade (1200 grade) was reached. Thereafter the samples were degreased with acetone and washed with running distilled water. In order to simulate the environment of the Gulf seawater, a modification was made on the typical electrochemical cell, to match the requirements of this study, by maximizing the cell's size to the limit, where no turbulence flow will occur due to the velocity of the incoming fresh seawater. Also, the cell was an open system to ensure having continuous fresh seawater coming into the cell, which is a typical case to form marine micro fouling on the surface of the samples.

The size of the electrochemical cell of this study was 100 cm length × 60 cm height × 40 cm width, and it was made of transparent plastic material, for the sake of visual inspection. At the top of the electrochemical cell (rectangular container), holes were made to insert the samples which were fitted with special Teflon, the calomel reference electrode (saturated potential of –241 mV/normal hydrogen electrode), and the counter electrode which was a graphite rod (Fig. 1). Filtered fresh gulf seawater was injected to the electrochemical cell continuously from the seawater intake of the Doha power and desalination plant in Kuwait. The effect of the marine micro fouling on the corrosion behavior of these alloys was examined by recording the open circuit potential values and EIS tests in flowing seawater as a function of time. Both mea-

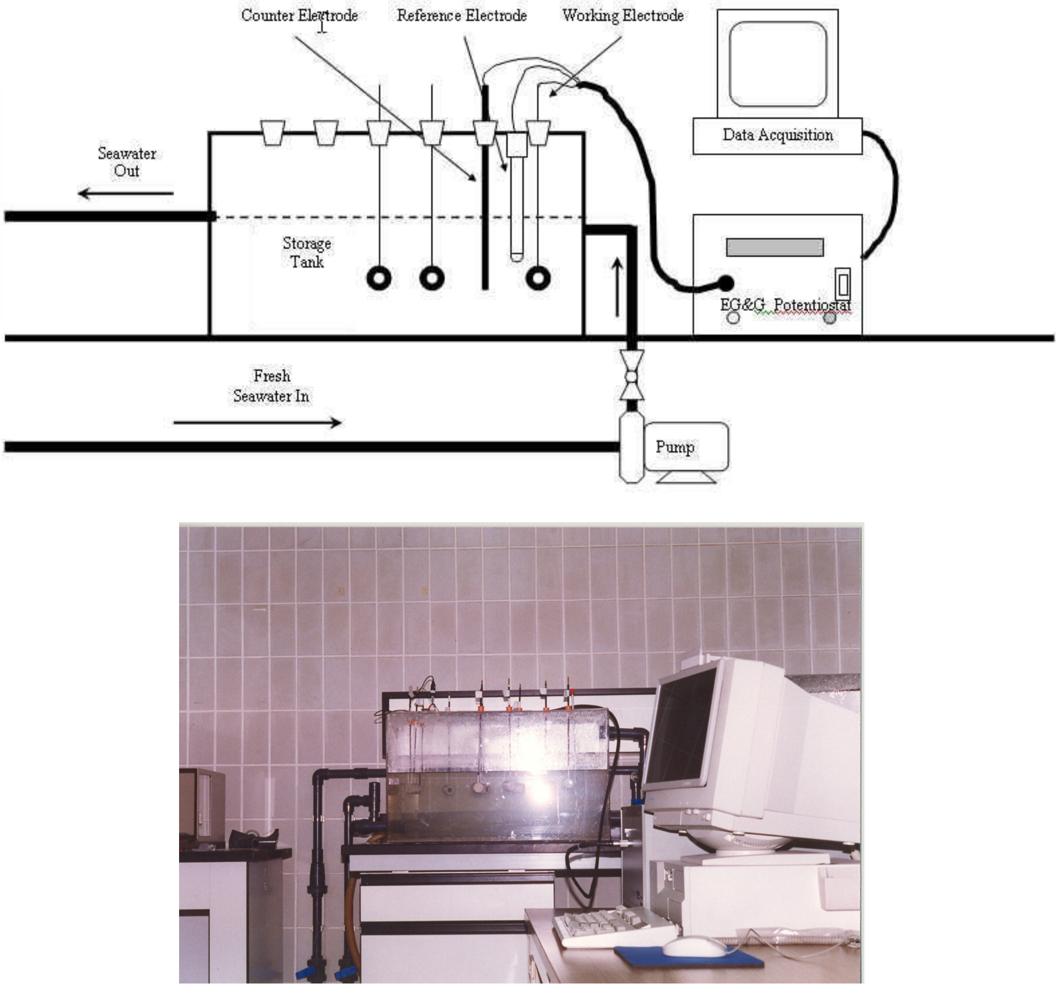

Fig 1. Experimental setup.

surements were carried out by using EG&G impedance analyzer-system model 6310. Furthermore, the outputs of the results were analyzed by the software EG&G 398. The initial frequency of the EIS was 100 KHz and, the final frequency was 10 mHz. These tests were carried out for the stainless steel alloys at 0 day, 1 day, 5 days, 1 month, 2 months, 3 months, 4 months, 5 months, and up to 6 months. In addition to the experiments of the effect of seasonal changes, separate experiments regarding the effect of residual pollutants in the Arabian Gulf Seawater on stainless steel alloys were conducted by adding 4 ppm chlorine (sodium hypochlorite) and 5 ppm ammonia (NH_4OH) to the seawater. The temperature of the seawater during the tests was recorded and it was varied from 18°C in winter days to 33°C in the summer days. The output data was defined in Bode formats, from these plots, parameters such as polarization resistance R_p, solution resistance RΩ, and double layer capacitance $C_{\mathrm{d.l.}}$ were manually calculated.

3.3. *Results and discussion*

3.3.1. Effects of seasonal changes of seawater

At the end of the tests, a biofilm was observed to form on all metal surfaces. The biofilm was basically a thin layer observed on the whole surface of the alloys. The formation of the microorganisms layer can be attributed to the variation of the seawater temperature at the Doha power and desalination plant, which was observed to vary between 18°C and 33°C, during the tests [10]. This variation in temperature is liable to influence the microbial processes. In fact, A.M. Shams El Din et al. [11] showed that biofilm formation in the Gulf seawaters collected during the same season thrived with a rise in temperature within the range 23–40°C, which was attributed to an increase of the activity of the microorganisms. It is worth to mention that, the corrosion of stainless steel caused by the microrganisms is due to the lack of oxygen under the microorganisms deposits area. This area becomes anode compared to the area with excess oxygen, leading to localized corrosion

Table 1
Average physical and chemical analysis of the fresh seawater in Doha research plant

Analysis (ppm)	Fresh seawater
pH	8.34
Total alkali	145
TDS	42,255
Na^+	13,493
K^+	443
Ca^+	515
Mg^+	1,570
Al^{2+}	1.16
F^-	1.53
Cl^-	22,185
SO_4^{2-}	3,154
Fe^{2+}	0.026
Sr^{2+}	7.41
Ba^{2+}	0.025
Cu^{2+}	0.025
HCO_3	143
CO_2	1.91
PO_4	0.025
NH_3	0.43
COD	400
BOD	6

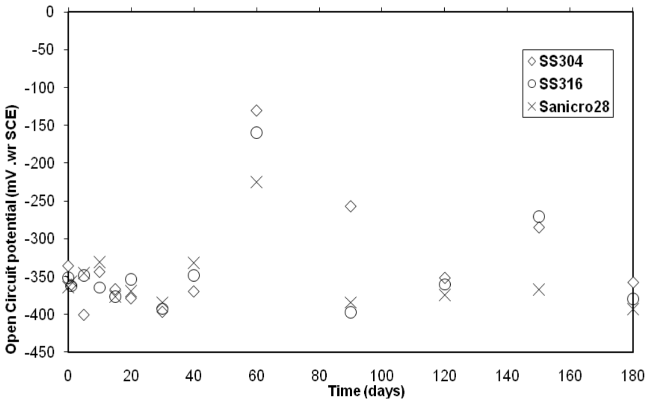

Fig. 2. Open circuit potential vs. time for different materials exposed to continuous flowing fresh seawater.

[12]. The potential-time curves of the tested alloys are given in Fig. 2. The data shows that SS304, SS316 and Sanicro 28 have stable potential values with time in the first 40 days which was at winter season, and became more positive for the next 2 months. This can be explained due to the slow rate of the biofilm formation during winter season, on the surface of the examined samples. On the other hand, the potential of the tested samples was observed to shift down (more negative) after 60 days of exposure. This was due to the warm up of the seawater, which consequently increased the rate of formation of the microorganisms on the surface of the tested samples. It is important to mention that, the OCP of SS304 and SS316 were shifted into positive direction (more noble). The OCP values of SS304 and SS316 were increased to –130 mV and –159 mV respectively, after 60 days of exposure. This phenomena which is related to the increase of the kinetics of the cathodic reaction, might be linked to the settlement of aerobic microorganisms colonizes formed on the surface of stainless steel samples. It has been suggested that, the enzymes within the biofilms is the responsible of the increasing of the cathodic reaction rate by producing oxidizing species, such as H_2O_2, MnO_2, and acid environments [13–16].

Figs. 3, 4 and 5 shows the Bode plots of impedance spectra for SS304, SS316, and Sanicro28 respectively, in flowing fresh seawater as a function of frequency at 0 day, 1 day, 5 days, 20 days, 30days, 60 days, 90 days, 120 days, 150 days, and after 180 days of exposure. The polarization resistance (R_p), and double layer capacitance (C_{dl}) were calculated from these plots, based on the average of three EIS tests, and are listed in Table 2. Table 2 shows that in the first 30 days of exposure when the seawater temperature was almost constant, very slight changes on the values of R_p, C_{dl} were observed for SS304 and SS316. After 60 days of exposure, the electrochemical impedance behavior of SS304 was shifted toward more resistive behavior with the decrease of the seawater temperature. Also, Table 2 shows that R_p increased from 9.8 KΩ.cm^2 to 121 KΩ.cm^2, and C_{dl} values decreased from 3.5 μF/cm^2 to 2 μF/cm^2. A behavior similar to this alloy was observed for SS316 as the R_p increased from 19 KΩ.cm^2 to 92 KΩ.cm^2, and C_{dl} value dropped from 1.5 μF/cm^2 to 0.83 μF/cm^2. On the other hand, the impedance parameters of SS304 and SS316 exhibited less corrosion resistance after 60 days of exposure, as the seawater temperature was observed to increase, which is in agreement with the OCP curve illustrated in Fig. 2. Data of the corrosion penetration rate with respect to the exposure time and temperature, under dynamic flow of fresh seawater, are listed in Table 2 by implementing Eqs. (1) and (2) and using the obtained values of the R_p, the values of corrosion rate of SS304 and SS316 are dependent on seasonal changes of the Arabian Gulf seawater, since the seasonal changes are known to alter the rate of microfouling formation on the surface of the tested samples. The corrosion rate for SS304 was observed to increase from 0.39 mpy to 1.145 mpy during the warm season of the gulf seawater, which occurred after 90 days of exposure. This can be explained due to the increase of the activity of microfouling, which subsequently increased the biofilm formation on the surface of SS304. Furthermore, the corrosion rate of SS316 was observed to decrease from 1.21 mpy to 0.129 mpy as the seawater temperature decreased from 25°C to 19°C. This

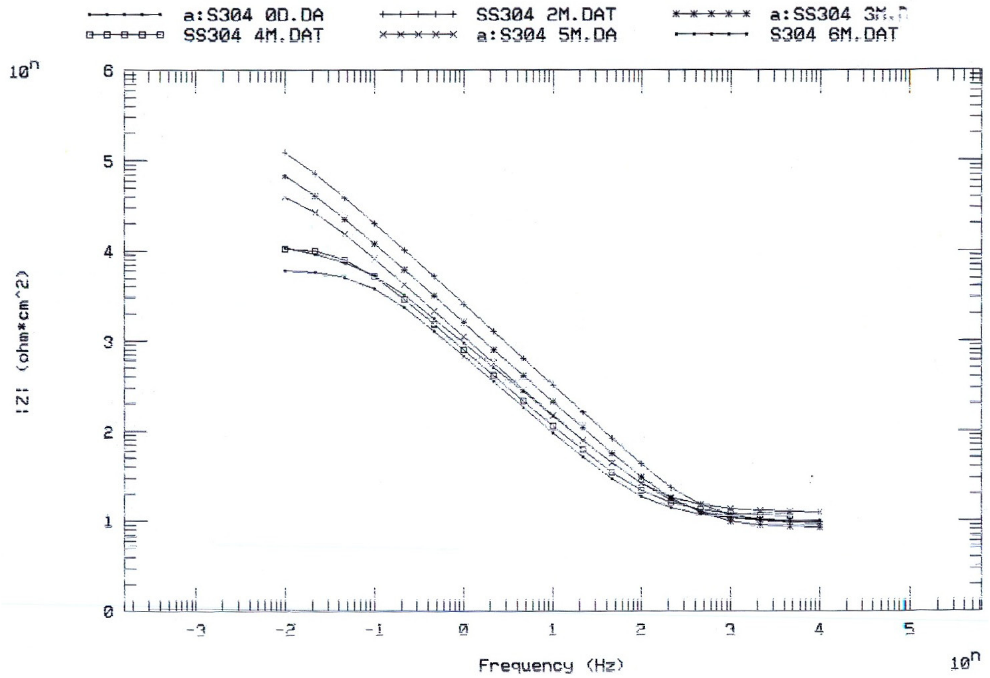

Fig. 3. Bode plots for stainless steel 304 from 0 to 180 days of exposure time.

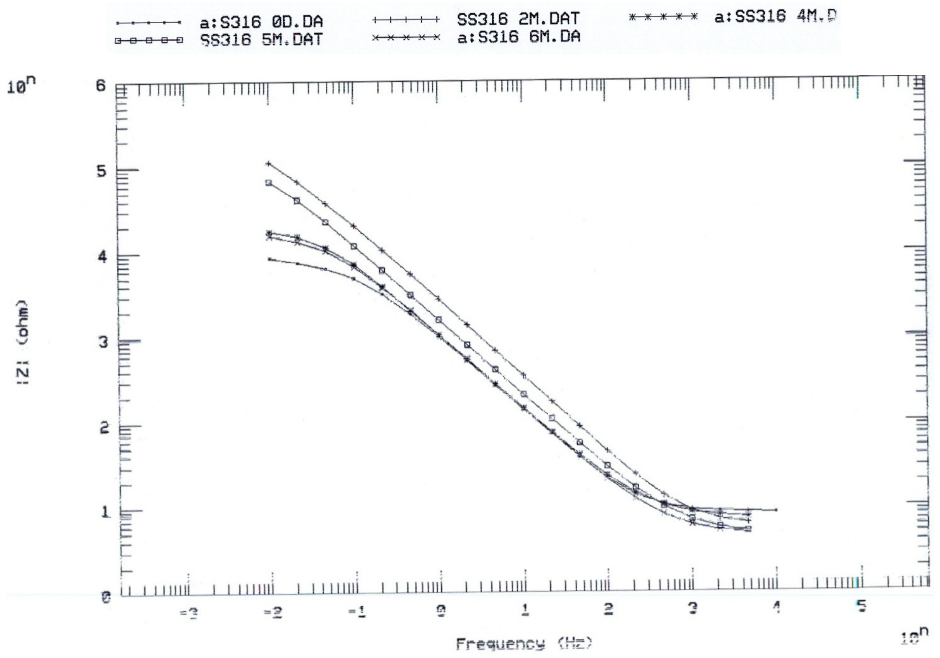

Fig. 4. Bode plots for stainless steel 316 from 0 to 180 days of exposure time.

can be interpreted by the reduction of the rate of the biofilm formation on the surface of SS316. Unlike SS304 and SS316, Sanicro 28 was not significantly influenced by the change of the growth rate of the microorganisms during the test. For example, at day 30 and day 60 of exposure the values of R_p had increased from KΩ.cm^{2}μF/cm^2 to 140 KΩ.cm^2, although the seawater temperature had decreased at that time, then after 90 days of exposure the value of Rp dropped to 44 KΩ.cm^2, with the warm up of seawater temperature. However, the Sanicro 28 double

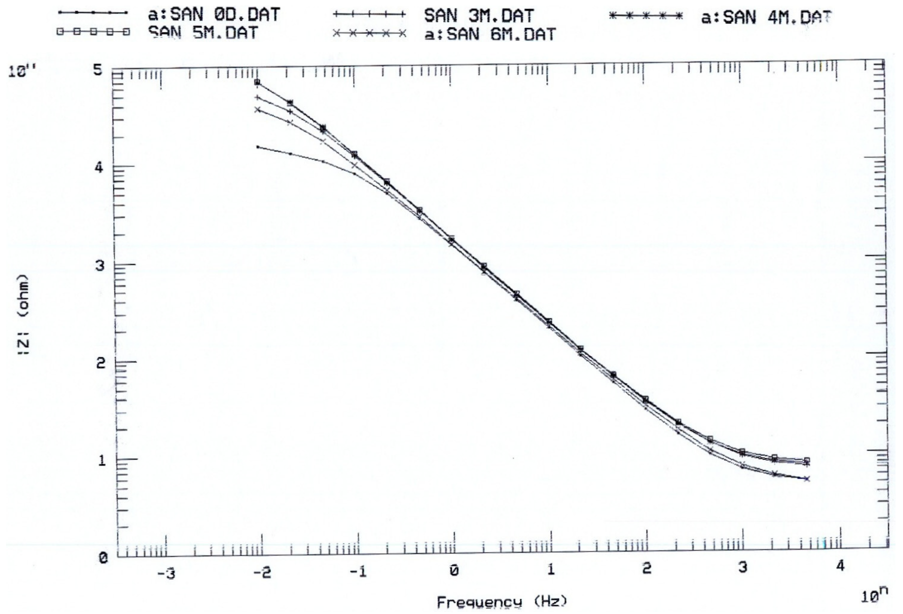

Fig. 5. Bode plots for Sanicro28 from 0 to 180 days of exposure time.

Table 2
Result of the average impedance parameters and corrosion rate for SS304, SS316, and Sanicro 28 as a function of time

Time (d)	Seawater temp. (°C)	R_p (KΩ.cm^2)			C_{dl} (μF/cm^2)			Corrosion rate (mpy)		
		SS304	SS316	Sanicro28	SS304	SS316	Sanicro28	SS304	SS316	Sanicro28
0	30	10	10	15	3.3	2.5	0.83	1.2	1.18	0.79
1	28	8.7	8.8	39.2	3.4	2.6	0.7	1.3	1.35	0.31
5	27	10.3	9.6	20.4	3.1	2.5	1	1.14	1.24	0.584
20	25	9.5	9.8		3.5	2.5		1.24	1.21	
30	22	9.8	19	31.8	3.5	1.4	0.9	1.21	0.63	0.377
60	19	121	92	140	2	1	0.52	0.1	0.129	0.083
90	23	65		44	0.5		0.6	0.39		0.271
120	25	10.3	16.9	65.7	1	1.5	0.59	1.145	0.71	0.18
150	27	105	64	70.4	0.5	0.83	0.58	0.11	0.12	0.17
180	31	10.1	15	35.73	3.1	0.5	0.69	1.18	0.11	0.336

layer capacitance values of were observed to be stable, and the corrosion rate values were low, and remained constant during the test.

The results of this work revealed the effect of the addition of molybdenum as alloying element in MIC resistance, which might be attributed to the role of molybdenum in decreasing the adhesion ability of the microorganisms colonies on the surface of stainless steel. For example, Sanicro 28 which has 3.5% Mo showed more corrosion resistance compared to SS316 which has 2.5% Mo, whereas SS304 which has no Mo in its content, showed the poorest corrosion resistance among the examined alloys. In addition to the effect of molybdenum on biofilm, some studies showed that the biofilm viable and total cell counts were found significantly higher on grade 304 stainless steel compared to pure molybdenum [17,18].

3.2. *Effect of residual pollutants*

Figs. 6, 7 and 8 represent Bode plots for SS304, SS316 and sanicro 28, respectively, for clean fresh seawater and modified seawater. Table 3 presents the values of seawater solution resistance, polarization resistance, double layer capacitance, and the corrosion rate parameters obtained from these plots, before and after the addition of chlorine and ammonia. The addition of chlorine to the water will

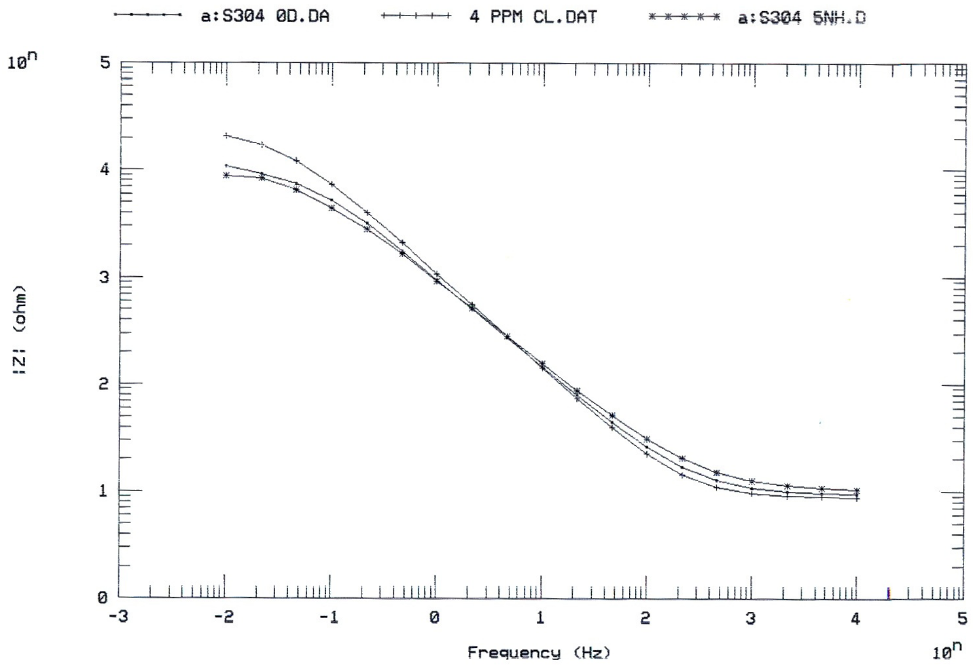

Fig. 6. Bode plot for stainless steel 304 in clean, chlorine, and ammonia modified flowing seawater.

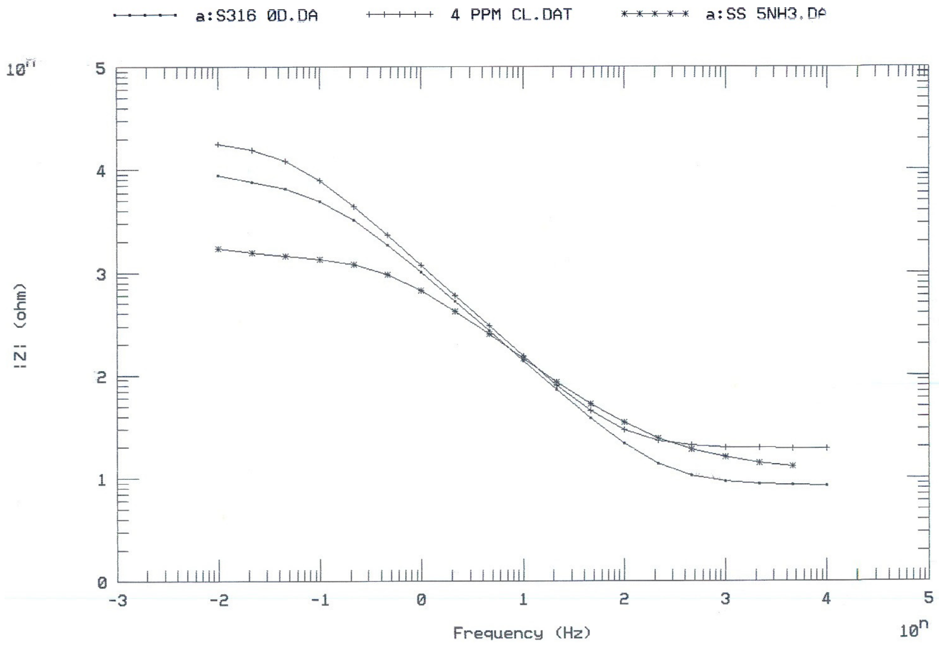

Fig. 7. Bode plot for stainless steel 316 in clean, chlorine, and ammonia modified flowing seawater.

produce hypochlorous acid, HOCL, which is a strong oxidizing agent and must be considered as a potential cathodic depolarizer. HOCL will oxidize bromide ions that present in seawater to bromine ions, which can cause severe corrosion to metals and alloys used in chlorinated seawater [19]. The results in Table 3 for SS304 show the polarization resistance increased upon the addition of 4 ppm chlorine to the seawater. The polarization resistance value for SS304 was 10 KΩ.cm^2 in clean seawater and 20 KΩ.cm^2 for chlorine modified seawater. As a result the corrosion rate of SS304 was decreased from 1.2 mpy to 0.577 mpy after the addition of chlorine. The double layer capacitance value of SS304 was observed to decrease after the addition of chlorine. Same corrosion behavior

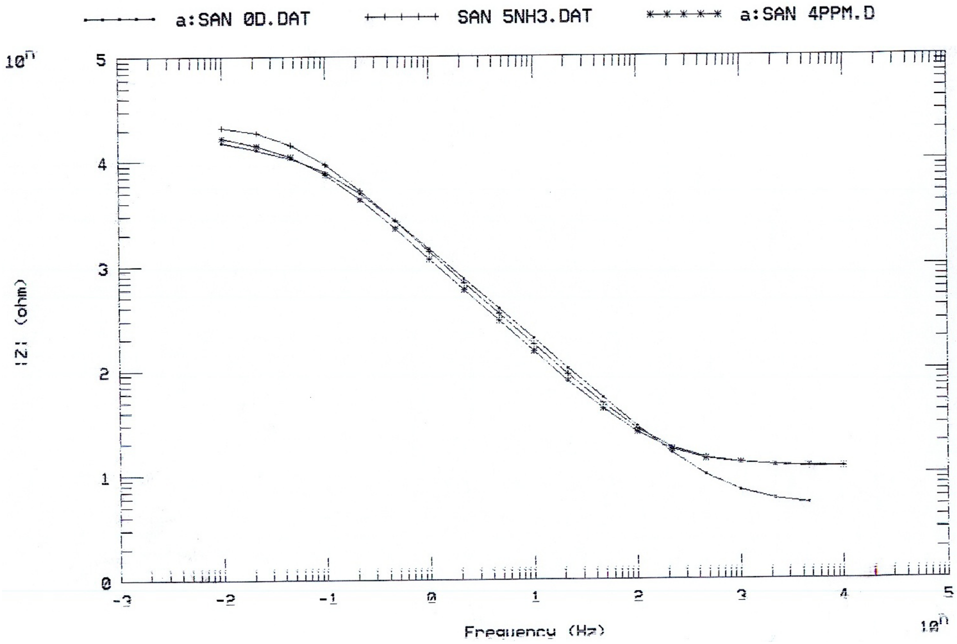

Fig. 8. Bode plot for sanicro 28 in clean, chlorine, and ammonia modified flowing seawater.

Table 3
EIS results for fresh seawater and modified seawater

Material	Media	R_{sol} (Ω.cm^2)	R_p (Ω.cm^2)	C_{dl} (μF/cm^2)	mpy
SS 304	Seawater	10.9	10.0	3.3	1.2
	4 ppm Cl_2	8.6	20.6	2.5	0.577
	5 ppm NH_3	10.36	8.4	10	1.4
SS 316	Seawater	10	10	2.5	1.18
	4 ppm Cl_2	33	19.12	3.3	0.62
	5 ppm NH_3	22	14.6	25	0.81
Sanicro 28	Seawater	5.64	15.0	0.95	0.796
	4 ppm Cl_2	18	14.5	0.83	0.82
	5 ppm NH_3	12	20.46	1.1	0.584

of the effect of chlorine on SS304 was observed on SS316 with the addition of chlorine to the seawater, whereas the double layer capacitance observed to increase after the addition of chlorine to the seawater. These unexpected results of the effect of chlorine, which is known as oxidizer, on the surface of SS304 and SS316, might be caused by the buildup of oxide or scale films on the surface of SS304 and SS316 due to the excess addition of chlorine. These oxide films are known to provide barrier to the oxygen access to the surface of the samples, and as a result the corrosion rate was observed to decrease. In addition, there were no significant changes observed on the surface of Sanicro 28 upon the addition of chlorine to seawater, which might be attributed to the formation of a passive film on the surface of the sample or to the rapid repassivation kinetics in dynamic flowing seawater. Table 3 shows that the corrosion resistance behavior was increased for SS304, and decreased for SS316 and Sanicro 28 upon the addition of ammonia to seawater. In addition, the double layer capacitance of the tested samples were observed to highly increase. The corrosion of material in ammonia polluted seawater system, is attributed to the formation of bromamines and chloramines, which are corrosive agents affecting the stability of the protective layers on alloys exposed to ammonia polluted seawater [20].

4. Conclusion

1. The measurements of the open circuit potential (OCP) clearly revealed the effect of the seasonal changes on

the corrosion potential of stainless steel 304, stainless steel 316 and Sanicro28.

2. Electrochemical impedance spectroscopy (EIS) technique was found to be a good tool to characterize the corrosion behavior, in terms of polarization resistance (R_p) and corrosion rate of metallic samples under hydrodynamic conditions. R_p and Icorr were extracted from Bode plots, which were obtained by EIS.
3. The polarization resistance of metallic sample extracted by EIS plots can be used to estimate the current density and the corrosion rate of metallic samples.
4. The seasonal change of the Gulf seawater was found to alter the polarization resistance of stainless steel 304 and stainless steel 316.
5. The seasonal changes of the Gulf seawater were found to influence the corrosion resistance of stainless steel 304 and stainless steel 316, due particularly to the change of seawater temperature, which affect the rate of microfouling formation or biofilm formation on the surface of the tested samples.
6. Sanicro 28 samples exhibit a higher corrosion resistance to the effect of the seasonal changes of the Gulf seawater than the other materials.
7. The excess addition of chlorine was observed to increase the corrosion resistance of SS304 and SS316. However the excess addition of ammonia caused no significant changes on the corrosion behavior of the examined alloys.

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