## The Mechanism of Alternating Current Corrosion of API Grade X65 Pipeline Steel

E. Ghanbari,\* M. Iannuzzi,\*\* and R.S. Lillard<sup>‡,\*</sup>

### ABSTRACT

In the present work, corrosion rates of API grade X65 pipeline steel in sodium chloride solutions with and without alternating currents (AC) at different direct current (DC) potentials were measured using weight loss analysis. The results show that the effect of AC is most pronounced near the open-circuit potential; at more positive potentials, the rates approach those of the ohmic drop/mass transport-limited DC rates. Correspondingly, at negative potentials the rates decrease. Surprisingly, it was found that at all potentials, the AC corrosion rate was equal to the average AC current in the system. The data generated from weight loss experiments were compared with the results from a model for AC corrosion that was developed using a modified Butler-Volmer approach. The model considers the anodic and cathodic Tafel slopes, diffusion limited oxygen transport, interfacial capacitance, and solution resistance. Both experimental and model results showed the importance of the interfacial capacitance on the rate of AC corrosion, especially at a frequency of 60 Hz. The models were also used to explain the observation that the AC corrosion rate was equal to the average AC current in the system.

KEY WORDS: alternating current (AC) interference, alternating current (AC) corrosion, capacitance, model, pipeline steel, solution resistance, Tafel slopes

### INTRODUCTION

Increased corrosion rate in the presence of alternating current (AC) has been known to occur for quite some time. As long as 100 years ago, investigators from the National Institute of Science and Technology described this in a paper titled, "Influence of Frequency of Alternating or Infrequently Reversed Current on Electrolytic Corrosion."<sup>1</sup> However, it was not until an accident on a pipeline in Germany in 1986 that it became a widespread industry topic and a safety concern. That failure occurred on a polyethylene-coated pipe installed parallel to a 16.6 Hz powered railway. The pipeline was cathodically protected at -1,000 mV vs. saturated calomel electrode (SCE) using an impressed current system, typical of European industry standards of the time.<sup>2</sup> It was concluded that a low soil resistivity of 1,900  $\Omega$ ·cm from deicing salts was a contributing factor in the failure. Since then, there have been numerous field cases of AC-induced failures in pipelines with otherwise adequate cathodic protection (CP).<sup>3</sup> As a result, international and U.S. standards, as well as "best practices," have been published detailing corrosion protection criteria to mitigate AC-induced corrosion on buried pipelines.<sup>3-6</sup> In addition to pipelines, the prospect of AC-induced corrosion has prompted the oil and gas industry to develop mitigation strategies for its subsea operations.<sup>7-8</sup> In that application, AC is used for autonomous operations, as well as to heat pipelines coming from the well to reduce the formation of hydrates and waxes.

To contribute to the development of standards, a large number of field studies have been performed to

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<sup>&</sup>lt;sup>+</sup> Corresponding author. E-mail: lillard@uakron.edu.

<sup>\*</sup> Chemical and Biomolecular Engineering, The University of Akron, Akron, OH 44325.

<sup>\*\*</sup> General Electric, Eyvind Lyches vei 10, Sandvika 1338, Norway.

characterize the variables that contribute to AC-induced corrosion on pipelines, such as: AC potential (or AC current), level of cathodic protection, and soil resistivity.<sup>9-14</sup> From these studies, it is generally agreed that, at the open-circuit potential (OCP), increasing AC pipe potential results in an increase in corrosion rate.<sup>15</sup> The effect of CP has also been examined for steel in a simulated soil solution containing  $Cl^-$ ,  $SO_4^-$ , and  $HCO_3^-$  salts and the data show a very clear relationship between CP potential and corrosion rate. While some protection is afforded at -0.85 V copper-copper<sup>2+</sup> sulfate electrode (CSE), it is not until the CP potential is reduced to  $-1.0 V_{CSE}$  that the effects of AC can be sufficiently mitigated.<sup>16</sup> The effect of additional CP is not known, however, and it has been proposed that overprotection of pipelines with an impressed AC may occur at these lower potentials, though this has not been confirmed.<sup>17</sup> Finally, as noted in the above German failure, there is a clear increase in AC corrosion risk with low soil resistivities.<sup>18</sup> While potential, CP, and soil resistivity are among the most important parameters, there are other variables that influence AC corrosion rates, such as surface scale that occur from the deposition of minerals such as calcium carbonates and hydroxides.<sup>11-20</sup>

Gellings was among the first researchers to model AC corrosion rates of metals.<sup>11</sup> In that work, the influence of parameters such as Tafel slope (i.e., activation vs. transport control) were used to develop a generalized expression to estimate weight loss. However, neither data nor model validation were presented. Chin, et al., proposed a preliminary theoretical approach to explain the polarization behavior of mild steel in a sodium sulfate solution with a superimposed AC potential.<sup>10</sup> In their model, a Butler-Volmer (B-V) style equation was used. While the comparison between the calculated polarization curves and the experimental results was limited at best, they reported oscillograms of the AC current response (current vs. time) as a function of frequency that showed a distortion in peak shape away from the "sinusoidal form." The magnitude of this distortion was a function of frequency; however, the frequency dependence was not explained by the authors. This paper will show that it may be attributed to the juxtaposition of the reactions occurring at the double layer, namely oxidation rate, reduction rate, and interfacial capacitance.

Other theoretical investigations worth mentioning include the work of Bertocci and later of Bosch, both of which used a B-V style expression of the form:<sup>9,21</sup>

$$i = i_{corr} \left[ e^{\frac{(E_{DC} + E_0 \sin(\omega t))}{\beta_a}} - e^{-\frac{(E_{DC} - E_0 \sin(\omega t))}{\beta_c}} \right]$$
(1)

where i is current density passing through the system,  $i_{\rm corr}$  is the corrosion current density in the absence of applied alternating voltage,  $E_{DC}$  is the applied DC

potential,  $\beta_a$  and  $\beta_c$  are anodic and cathodic Tafel slopes,  $E_0$  is the peak potential, and  $\omega$  is the angular frequency of the AC signal. Equation (1) assumes activation control and does not consider potential drop across the solution resistance or the effect of double layer capacitance. However, Bosch, et al., were among the first researchers who considered the effect of diffusion phenomena on corrosion rate with applied AC potential.<sup>9</sup> In their analysis, they assumed that AC and DC polarizations do not influence each other and as a result, concentration of oxidants at the electrode surface consists of two separate DC and AC parts. Based on their model, Bosch, et al., concluded that the increase in the corrosion rate was limited by the diffusion-limited current density. This conclusion will be rebutted in this paper.

In comparison, Lalvani, et al., proposed a model that considered both potential drop across the solution resistance and the effect of double layer capacitance.<sup>22</sup> In that model a simple Randles' circuit was assumed, where the total potential drop in the system  $(E_T)$ , was the sum of DC and AC potentials:

$$E_{\rm T} = E_{\rm DC} + E_0 \sin \omega t \tag{2}$$

In this model,  $E_T$  was equal to the sum of the potential drop across the electrochemical interface (E) plus the potential drop across the solution resistance ( $R_s$ ):

$$E_{\rm T} = E + i_{\rm T} R_{\rm s} \tag{3}$$

The total current flow  $(i_T)$  across the interface was defined as the sum of the capacitive current  $(i_c)$  and the Faradaic current  $(i_F)$ :

$$\mathbf{i}_{\mathrm{T}} = \mathbf{i}_{\mathrm{c}} + \mathbf{i}_{\mathrm{F}} \tag{4}$$

where  $i_{\rm F}$  is the sum of the anodic (i\_o) and the cathodic (i\_r) currents,

$$\mathbf{i}_{\mathrm{F}} = \mathbf{i}_{\mathrm{o}} + \mathbf{i}_{\mathrm{r}} \tag{5}$$

The current flow through the interfacial capacitance  $(C_i)$  was defined as:

$$i_{\rm c} = C_{\rm i} \frac{\mathrm{dE}}{\mathrm{dt}} \tag{6}$$

Substituting Equations (6) and (5) into Equation (4) and further combination of the result with Equations (2) and (3) yielded a general expression for the potential drop across the interface:

$$\frac{\mathrm{dE}}{\mathrm{dt}} + \frac{\mathrm{E}}{\mathrm{C}_{\mathrm{i}}\mathrm{R}_{\mathrm{s}}} + \frac{\mathrm{i}_{\mathrm{o}} + \mathrm{i}_{\mathrm{r}}}{\mathrm{C}_{\mathrm{i}}} = \frac{\mathrm{E}_{\mathrm{DC}} + \mathrm{E}_{\mathrm{0}}\,\sin\,\omega\mathrm{t}}{\mathrm{C}_{\mathrm{i}}\mathrm{R}_{\mathrm{s}}} \tag{7}$$

Lalvani, et al., also considered both anodic and cathodic reactions under activation control. In their

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model, the values of  $i_{\rm o}$  and  $i_{\rm r}$  had their traditional Tafel definitions:

$$i_{o} = i_{corr} e^{\frac{(E-E_{corr})}{\beta_{a}}}$$
 (8)

and

$$\mathbf{i}_{\mathrm{r}} = \mathbf{i}_{\mathrm{corr}} \, \mathrm{e}^{-\frac{(\mathrm{E} - \mathrm{E}_{\mathrm{corr}})}{\beta_{\mathrm{c}}}} \tag{9}$$

where  $E_{corr}$  is the corrosion potential measured in the absence of AC.

Substituting Equations (8) and (9) into Equation (7) led to their final nonlinear differential equation for E:

$$\frac{dE}{dt} + \frac{E}{C_{i}R_{s}} + \frac{i_{corr}e^{\frac{(E-E_{corr})}{\beta_{a}}} + i_{corr}e^{\frac{-(E-E_{corr})}{\beta_{c}}}}{C_{i}}$$
$$= \frac{E_{DC} + E_{0}\sin\omega t}{C_{i}R_{s}}$$
(10)

Lalvani, et al., obtained numerical solutions for Equation (10) using two different methods, one using a linear model and the other using a perturbation method.<sup>22-23</sup> Based on their models, it was concluded that the corrosion current would be lower at higher frequencies, in agreement with experimental data.<sup>24</sup> For the perturbation analysis, they assumed that the ratio of DC corrosion current to the double layer capacitance value is much lower than unity and, therefore, could be neglected.<sup>22-23</sup> As a result of assumptions in their numerical solution, the DC potential does not have any influence on AC corrosion rates, which is in contrast with the results obtained by others.

In this paper, the mechanism of AC corrosion of API grade X65 pipe steel in sodium chloride solution is investigated, presenting corrosion rate data with and without AC potentials. To explain the trends observed as a function of AC potential, frequency, and applied DC potential, a model is developed, building on the work of Lalvani and Equation (7).<sup>22</sup> Factors addressed by the new model that previous models have omitted include: the effect of solution resistance, mixed cathodic reactions such as transport limited oxygen reduction, and hydrogen evolution.

## EXPERIMENTAL PROCEDURES

#### Electrode and Solution

The samples used in this work were fabricated from an API grade X65 (UNS K03014)<sup>(1)</sup> pipe steel. The chemical composition of the material was: C 0.04 wt%, Si 0.2 wt%, Mn 1.5 wt%, P 0.011 wt%, S 0.003 wt%, Mo 0.02 wt%, and Fe balance. The steel was in the quenched and tempered condition. The steel coupons

were cut into  $15 \times 12 \times 5$  mm samples with a tapped hole in one end for electrical connection via a threaded rod. Samples were ground with SiC papers, starting from 120 grit to 600 grit, and rinsed with acetone, ethanol, and distilled water, sequentially.

All tests were conducted in 0.1 M NaCl. The solution volume was 300 mL and was made from analytic grade reagents and 18.2  $M\Omega \cdot cm^2$  deionized water. All tests were conducted at ambient temperature (22°C) and open to air. To assess the effect of ferrous/ferric ion content and solution pH on corrosion behavior, three different conditions were examined: (i) static solution, (ii) intermittent batch replacement of solution (250 mL after each hour), and (iii) constant solution replacement at a rate of 8 mL/min. Replacement of solution was performed using a peristaltic pump, and to ensure the cell was mixed, solution stirring at 60 rpm was used. During the test, an aliquot of solution was taken periodically to measure pH and Fe ion content. In those tests, ultraviolet visible spectrophotometer (UVS) was used to determine ferrous ( $Fe^{2+}$ ) and ferric ( $Fe^{3+}$ ) ion concentration. The Fe<sup>3+</sup> content was indirectly obtained by calculating the Fe<sup>2+</sup> concentration, followed by a separate determination of the Fe<sub>Total</sub> concentration.<sup>25-26</sup> Before electrochemical measurements, the working electrode (WE) was kept in the test solution for 24 h at the OCP to ensure steady state.

All tests were performed in triplicate to ensure the reproducibility of the results.

#### Electrochemical Setup

Electrochemical measurements were performed using a PAR 273A<sup>†</sup> potentiostat in a conventional threeelectrode setup. A platinum mesh was used as counter electrode (CE) and a SCE as reference (RE). A Luggin capillary was used to prevent cross-contamination. The distance between the Luggin capillary and WE was approximately 15 mm, while the distance between the CE and WE was approximately 40 mm. In some photographic images, the distance between all electrodes was decreased to capture them in the same frame but no data were reported for these decreased distances: they are for photographic clarity only.

Potentiostatic tests were performed at potentials of -720, -700, -670, -600, -500, -440, and 0 mV<sub>SCE</sub> with and without impressed AC potentials. The AC signal was generated using a Solartron 1255 Frequency Response Analyzer<sup>†</sup> (FRA). In this configuration, the signal output from the FRA was connected to the external input of the potentiostat. Thus, the AC signal could be applied between RE and WE through the potentiostat at a constant potential "on top" of the applied DC. AC root mean square (RMS) potentials of 100, 200, 300, 400, 500, and 600 mV at a frequency of 60 Hz were used. These nominal signal generator potentials and the actual values (as measured by the FRA) varied between 10% and 20% depending on magnitude.

<sup>&</sup>lt;sup>(1)</sup> UNS numbers are listed in *Metals and Alloys in the Unified Numbering System*, published by the Society of Automotive Engineers (SAE International) and cosponsored by ASTM International. <sup>†</sup> Trade name.

In order to investigate the effect of AC frequency on corrosion rate, tests at the OCP using lower frequencies (0.01, 0.1 and 1,000 Hz) were performed. The current-time and potential-time response under various DC and AC potentials were recorded with an acquisition rate of 0.1 points per second for low frequencies (i.e., 0.01 Hz and 0.1 Hz), while higher frequencies (i.e., 60 Hz and 1,000 Hz) were collected at a rate of 250 points per second. Electrochemical impedance spectroscopy (EIS) data were taken after each experiment with and without AC at OCP in order to monitor the solution resistance value. The frequency scans were taken from 100 kHz down to 0.01 Hz with 10 mV AC amplitude.

Weight loss analysis was conducted in accordance with ASTM Standard G1.<sup>27</sup> Immersion time was varied depending on anticipated weight loss and resolution of the balance. For example, for higher RMS AC potentials and or DC potentials, the initial immersion time may have been as short as 2 d. For lower AC potentials and or cathodic DC potentials, the immersion time was up to 3 weeks. After potentiostatic tests, the corrosion product formed on the coupon surface was removed by both mechanical and chemical methods as described in the standard. The mechanical method included scrubbing with a nylon brush and was used to remove loosely adhered corrosion product. To remove tightly bound oxide films, samples were immersed several times for 25 s in Clarke's solution: concentrated HCl (specific gravity 1.19), 2 wt% Sb<sub>2</sub>O<sub>3</sub>, and 5 wt% SnCl<sub>2</sub>.

### **RESULTS AND DISCUSSION**

### Effect of Solution Composition on Corrosion Rate

Given that the immersion period of the weight loss experiments was relatively long, there was concern that the change in solution properties over time would make interpretation of the results difficult.<sup>28-34</sup> For example, sustained cathodic reactions over a period of days in the relatively small volume could have significant effects on solution pH.<sup>28-32</sup> In addition, if the corrosion rates were high, in some cases large amounts of dissolved Fe<sup>2+</sup> could accumulate in the cell. As each of these factors can influence corrosion rates in pipeline steels,<sup>33-34</sup> a series of experiments were designed to optimize solution composition. Figure 1 shows the variation in current density resulting from changes in the chemical composition of the electrolyte without solution replenishment and stirring. Each solid symbol represents data points obtained from the mean steady state current density value from potentiostatic steps at constant DC potential. The solid line represents data taken using the potentiodynamic polarization method (stirred and replenished only).

As seen in Figure 1, current densities obtained from samples in the stagnant solution were consistently lower than those obtained using solution



FIGURE 1. Effect of solution replenishment and stirring on current density.

replenishment. UVS analysis of aliquots of solution at anodic potentials and solution pH versus charge passed are presented in Figure 2. Charge passed was used as opposed to time, as it is a better reflection of what is occurring on the corroding sample; for example, one would anticipate larger Fe<sup>2+</sup> concentrations in a stagnant solution with larger charge passed. In contrast to the stagnant solution, solution replenishment/stirring resulted in constant Fe<sup>3+</sup> concentration over the course of the immersion period (Figure 2[a]) and relatively constant pH values of approximately pH = 7.0. Therefore, the lower current density without solution replenishment/stirring was attributed to the combination of pH and Fe<sup>3+</sup> that decreases corrosion rate.<sup>28-34</sup> In the remainder of the work, the decision was made to use solution stirring and replacement to eliminate any external influences other than imposed AC potential on corrosion behavior of carbon steel.

## Influence of Combined Alternating Current and Direct Current Potentials on Corrosion Rate

Figure 3 compares corrosion rate with and without AC (RMS voltage = 600 mV and f = 60 Hz) as a function of DC potential. Results were obtained by weight loss analysis after the potentiostatic test. The values of mass loss obtained at each of the DC biases were converted to equivalent current densities using Faraday's law:

$$i = \frac{m \cdot F}{t \cdot \rho} \tag{11}$$

where i is current density, m is the mass loss value, F is Faraday's constant equal to 96,485 C/mol, t is total exposure time, and  $\rho$  is density of carbon steel (7.8 g/cm<sup>3</sup>).

Weight loss was chosen as it was unclear if the current reported by the potentiostat would reflect the true Faradaic current in the system with an applied AC



**FIGURE 2.** Effect of solution replenishment and stirring on: (a) Fe content of the electrolyte at  $DC = -500 \text{ mV}_{SCE}$  and (b) pH of the electrolyte at  $DC = 0 \text{ V}_{SCE}$ .

signal. In other studies where potentiostats have been used to measure corrosion current polarization curves and linear polarization resistance (LPR), investigators have used separate AC and DC loops. In those



FIGURE 3. Effect of AC potential on corrosion rate of carbon steel at different DC biases.

investigations, an AC voltage was applied between the sample WE and a CE that was separate from the potentiostat CE, while the potentiostat was used to apply a DC potential between the WE and RE. However, an inductor (of the order of 10 H) was placed between the potentiostat and its CE, preventing the potentiostat from "responding" to the potential fluctuations on the WE created by the AC voltage. The result was that only DC current flowed in the potentiostat loop. This type of circuit was first used by Chin and later by Goidanich and others.<sup>10,35-36</sup> The use of an inductor in the potentiostat CE is fundamentally flawed, as the AC current generated by the oxidation reaction (above and beyond the oxidation current produced by the DC potential) is not measured by the potentiostat when an inductor is used. For example, consider the current response of the WE to a 60 Hz AC perturbation at a given applied DC potential assuming the electrode can be modeled as a simple resistor (e.g., a polarization resistance). In addition to the DC Faradaic current in the system, Faradaic current at 60 Hz will flow through the circuit: recall for an AC potential across a resistor  $Z(\omega) = R$ . The actual corrosion rate is the sum of these two Faradaic current contributions. However, in setups that use an inductor in the potentiostat CE, the Faradaic component of the AC signal is not part of the current measured by the potentiostat. As such, polarization curves, or LPR measured with an inductor in the CE, provide no information with respect to corrosion rate of the sample resulting from the imposed 60 Hz AC voltage. Faradaic and non-Faradaic currents are addressed further in this paper.

Figure 3 shows the effect of AC potential on corrosion rate of API grade X65 steel. Each data point in this figure represents the average of 3 independent weight loss measurements. As seen in Figure 3, both data sets with and without AC showed the same trend of increasing corrosion rate with increasing DC potential above  $E_{corr}$ . In addition, the corrosion rate in the presence of AC was greater at any given DC bias; for example, the corrosion rate at OCP (-670 mV) with AC was about 10 times higher than that without AC, consistent with observations made by other authors.<sup>35,37</sup> These results, along with the potentiodynamic polarization data shown in Figure 1, are compared in Figure 4. As seen in Figure 4, the current densities from mass loss without AC agreed well with the polarization curve. In addition, Figure 4 suggests that at very high DC biases, as the system approaches a combination of mass transport and IR control, the effect of AC was negligible. Finally, while it appears that there is a "shift" in the  $E_{corr}$  during AC, this is a fundamentally incorrect way of viewing the data. The AC signal is an impressed voltage that does not require the oxidation and reduction reactions to be occurring at steady state. There will be a potential at which the magnitude of the oxidation reaction during the positive portion of the sine wave will be equal to the reduction



**FIGURE 4.** Effect of AC potential on current density of carbon steel at different DC biases.

reaction; however, this is not the same as  $E_{corr}$ , as the source of current is not the opposing reaction, rather, the remote power source driving the AC signal. The potential at which this crossover point occurs depends on the relative magnitudes of the anodic and cathodic Tafel slopes, which is discussed later.

To better understand the relationship between AC, applied DC, and corrosion rate, mass loss experiments as a function of applied DC and AC potential were conducted (Figure 5). As seen in Figure 5, corrosion rates decreased with decreasing AC RMS potential at any given DC potential. In addition, there was a decreasing trend in the AC:DC corrosion ratio with increasing DC potentials for all AC RMS levels, with the exception of the OCP. Near the OCP, the effect of AC was more pronounced as compared to more positive applied DC potentials. It is believed that this trend is a result of a combination of two factors: the magnitude



FIGURE 5. Effect of different RMS values on the ratio of corrosion rate with AC to the corrosion rate without AC at different DC potentials.

of the non-Faradaic (capacitive) current and the solution resistance.

# Alternating Current Potentials and Faradaic Currents

One way of analyzing the corrosion rate data obtained herein is to compare it with the total AC current in the system. Nominally, the total AC current varies with time at 60 Hz and can be separated into three categories: (1) the average positive AC current (AC(+)), which is the time averaged value of all of the current that is greater than zero; (2) the average negative AC current (AC(-)), which is the time averaged value of all of the current that is less than zero; and (3) the average AC current (AC(avg)), which is the time averaged value of all current (Figure 6[a]). Figure 6(b) compares the current density calculated from mass loss with AC(+), AC(-), and AC(avg). As seen in this figure, the weight loss data diverges sharply from AC(+), an indication that not all of AC(+) contributes to corrosion reactions; that is, not all of the AC(+) is Faradaic. In comparison, the weight loss data agreed almost exactly with the AC(avg). In fact, the data agreed so well most of the points overlapped.

While this phenomenon has been observed before for 60 Hz, it has not been explained.  $^{38-39}$  It is



**FIGURE 6.** (a) Schematic of sinusoidal AC current density from potentiostatic test and (b) comparison of current density with 60 Hz AC (RMS = 600 mV at different DC biases) from weight loss and AC(+), AC(-), and AC(avg).

proposed that this finding is specific to mid-range frequencies (1 Hz to 100 Hz) and occurs because the Faradaic current generated by the cathodic reaction is negligible as compared to the anodic reaction. To evaluate this, consider the equivalent circuit in Figure 7(a) that includes elements for the solution resistance  $(R_s)$ , the oxidation and reduction charge transfer resistances (Ro and Rr), and the interfacial capacitance ( $C_i$ ). Here, it is assumed that  $R_o$  and  $R_r$  are acting as voltage-controlled nonlinear resistors. Specifically, R<sub>o</sub> is related to the anodic Tafel slope  $(\beta_a)$  and  $R_r$  is related to three parameters: (1) the slope of the oxygen reduction reaction ( $\beta_c$ ), (2) the transport limited oxygen reduction current density  $(i_{I})$ , and (3) the slope of the hydrogen reduction reaction ( $\beta_{H_0}$ ). Both oxidation current (Faradaic) and capacitive current (non-Faradaic) occur during the positive halfcycle of the applied AC signal. Similarly, reduction and capacitive currents coexist during the negative half cycle of the applied AC signal. The magnitude of AC(+), Faradaic plus capacitive current, depends on the values of R<sub>o</sub> and C<sub>i</sub> (e.g., the RC time constant) and the frequency of the AC signal. Correspondingly, the values of R<sub>r</sub> and C<sub>i</sub> act independently to control the magnitude of AC(-). With respect to the capacitive current, the





FIGURE 7. (a) Full equivalent circuit for an electrode exposed to an AC potential and (b) reduced circuit when the cathodic reaction is relatively small with respect to the anodic reaction (i.e., mass transport limited oxygen reduction).

magnitude of the positive and negative half-cycles are equal and, as such, sum to zero. However, the Faradaic current generated by the oxidation and reduction reactions is independent. Thus, the value of AC(avg) is controlled by the rates of these two reactions. In the case of API grade X65 pipe steel in seawater, the value of  $R_r$  is high relative to  $R_o$  ( $\beta_a = 0.089$ ,  $\beta_c = 0.352$ , and  $\beta_{H_2} = 0.205$ ). As a result,  $i_o + i_r$  resembles  $i_o$ . For this reason, AC(avg) approximates the corrosion rate as measured by weight loss, as observed in Figure 6. The net result is that the circuit in Figure 7(a) reduces to the one shown in 7(b). There would be a similar result if there was a cathodic DC bias on the system and the applied AC potential was large enough to make  $i_o$  more significant than the  $i_r$ .

The effect of the RC time constant ( $R_rC_i$  and  $R_oC_i$ ) on AC(avg) and  $i_o$  (mass loss) can be seen in the data collected at lower frequencies. In Figure 8, the current values calculated from mass loss for API grade X65 steel in chloride solution exposed to an AC (600 mV RMS) and a DC potential of 0.17 V<sub>SCE</sub> vs. OCP are plotted as a function of frequency. As seen in Figure 8, as frequencies decreased from 60 Hz to 0.01 Hz, there was less agreement between mass loss and AC(avg) and better agreement between mass loss and AC(+). This occurs because at low frequencies  $i_C$  goes to zero, while  $i_o$  and  $i_r$  reached their maximum values. Because  $i_o > i_r$ , AC(+) approximates the mass loss data and AC(avg) with  $i_r$  now a measureable "error" in the approximation.

At low frequencies, the mechanism of AC-induced corrosion is visible on the electrode surfaces as periodic cycling of bubbles. Figures 9(a) through (f) present photographs of both the WE and CE surfaces as a function of time during an experiment at OCP for f = 0.01 Hz and AC = 600 mV RMS. The electrodes in the cell have been reconfigured for photographing, resulting in an aberrant RE position and decreased



**FIGURE 8.** Comparison of current density with 60 Hz AC (RMS = 600 mV and DC = -500 mV) from weight loss and AC(+), AC(-), and AC(avg) at different frequencies.



FIGURE 9. (a) through (f) Snapshots of the surfaces of working and counter electrode, (g) i-t curve, and (h) E-t curve during the experiment with AC (at OCP, RMS = 600 mV) in one cycle at 0.01 Hz, along with (i) schematic of the polarization curve without AC.

solution resistance. As can be seen in Figure 9(a), at the beginning of the sine wave there was a small positive current and corresponding low density of hydrogen bubbles on the CE surface. At the maximum potential of the WE, the density of hydrogen bubbles on the CE reached a maximum (Figure 9[b]). As time continued, the AC potential on the WE decreased, as did the hydrogen bubble density on the CE (Figure 9[c]). At approximately 60 s, the WE changed from anodic potentials to cathodic; Figure 9(d) shows the corresponding image of the WE during oxygen reduction. As the WE potential became more negative, the electrode fell below the reversible hydrogen potential and hydrogen bubbles began to form on the WE surface. This periodic cycling of the WE surface maps the polarization curve of API grade X65 pipe steel in seawater. To demonstrate this, points corresponding to the photographs of the cell are plotted on the experimental current vs. time and potential vs. time curves (recorded simultaneously) in Figures 9(g) and (h), respectively. These same points are plotted on the experimental polarization curve in Figure 9(i). It is seen in these figures that the cell current induced by the applied AC potential was proportional to the reaction rate at the WE, as indicated by the polarization curve of API grade X65 pipe steel. This effect is most pronounced at cathodic potentials where there is a combination of transport limited oxygen reduction and hydrogen evolution. For comparison to the low-frequency data in Figure 9, similar data at 60 Hz were also collected (not shown). Unlike the lower frequency data, there was limited hydrogen reduction on the WE in these experiments. This likely occurred because the total AC current at this frequency was predominantly non-Faradaic (capacitive) and the reduction current was small, which is addressed in the Model Development section.

From these results, it was concluded that an applied AC potential across an electrochemical interface polarizes the electrode as a function of time away from its DC potential along its polarization curve. The net effect of this polarization depends on a number of variables including: AC frequency, AC potential, Tafel slopes, interfacial capacitance, solution resistance, and applied DC potential. For carbon steel in sodium chloride solution where there is a low anodic Tafel slope, transport limited oxygen reduction, low solution resistance, and high interfacial capacitance. For example, a 600 mV, 60 Hz AC signal results in increased corrosion rates at all DC potentials investigated here, greater than  $-0.25 V_{OCP}$ .

#### MODEL DEVELOPMENT

In this section a new model is presented to predict corrosion rates of carbon steel in the presence of an AC potential. The model is, in part, based on the work by Lalvani (Equation [10]).<sup>22</sup> One of the assumptions in Equation (10) is that the Faradaic currents  $i_o$  and  $i_r$  can be described by activation control. However, at moderate

overpotentials and near-neutral solutions, the cathodic reaction is typically controlled by diffusion limited oxygen reduction  $(i_{r,O_2})$ , while at lower potentials by hydrogen evolution  $(i_{r,H_2}$ , Equation [12]). As such, a modified B-V function is presented that describes the anodic reaction under activation control, while the cathodic reaction is assumed to be under mixed control:

$$i_r = i_{r,O_2} + i_{r,H_2}$$
 (12)

where the mass transport limited oxygen reduction rate is governed by the expression:  $^{\rm 40}$ 

$$i_{r,O_2} = i_{corr} \frac{e^{2.3\frac{(E-E_{corr})}{\beta_c}}}{1 - \frac{i_{corr}}{i_c} + \frac{i_{corr}}{c} e^{2.3\frac{(-E+E_{corr})}{\beta_c}}}$$
(13)

where  $i_L$  is the limiting current density of oxygen reduction and the remaining terms take the usual meaning. The hydrogen evolution reaction rate is governed by the Tafel equation (Equation [14]):<sup>41</sup>

$$i_{r,H_2} = i_{0H_2} e^{2.3\frac{(-E+E_0)}{\beta_{H_2}}}$$
 (14)

where  $i_{0H_2}$  is hydrogen exchange current density and is a function of the nature of the cathode,  $E_0$  is the hydrogen standard equilibrium potential that is equal to zero in the standard hydrogen scale (SHE), and  $\beta_{H_2}$  is the Tafel slope of the hydrogen evolution reaction.

Substituting Equations (13) and (14) in Equation (12) and the combination of Equations (6), (10), and (12) leads to the nonlinear equation for potential drop (E) across the Faradaic resistance:

$$\frac{\mathrm{dE}}{\mathrm{dt}} + \frac{\mathrm{E}}{\mathrm{C}_{\mathrm{i}}\mathrm{R}_{\mathrm{s}}} + \frac{\xi}{\mathrm{C}_{\mathrm{i}}} = \frac{\mathrm{E}_{\mathrm{DC}} + \mathrm{E}_{\mathrm{0}}\,\sin\,\omega\mathrm{t}}{\mathrm{C}_{\mathrm{i}}\mathrm{R}_{\mathrm{s}}} \tag{15}$$

where

$$\begin{aligned} \xi &= i_{corr} \left( e^{2.3 \frac{(E-E_{corr})}{\beta_a}} - \frac{e^{2.3 \frac{(E+E_{corr})}{\beta_c}}}{1 - \frac{i_{corr}}{i_l} + \frac{i_{corr}}{i_l}} e^{2.3 \frac{(-E+E_{corr})}{\beta_c}} \right) \\ &+ i_{0H_2} e^{2.3 \frac{(-E-0.244)}{\beta_{H_2}}} \end{aligned}$$
(16)

### MODEL RESULTS

Even though the number of assumptions in Equation (15) has been minimized, finding the analytical solution for this expression would be very difficult. Thus, a numerical solution using MATLAB<sup>†</sup> software and ODE23S<sup>†</sup> solver based on Runge-Kutta Fehlberg method was used.<sup>42</sup> Using the potential drop across the Faradaic resistance from Equation (15), one may easily calculate the time averaged of oxidation current density (i<sub>o</sub>-model) along with the total current density passing through the system. Specific details are available in the Appendix.



**FIGURE 10.** Comparison of experimental mass loss data at 60 Hz and the solution of the Equation (15) for two different capacitance values (0.01 F and 0.001 F).

## Relationship Between Average Current and Mass Loss

It was shown in Figure 6 that AC(avg) agreed well with mass loss data. Figure 10 compares  $i_0$  from the model for two different capacitance values with the current densities obtained from experimental data. The other input values used for solving Equation (15) can be found in Tables 1 and 2. These values were obtained from IR corrected polarization data without AC (i.e., anodic and cathodic Tafel slopes, corrosion current density, corrosion potential, and oxygen limiting current density shown in Table 1), and EIS data. For applied potentials greater than the OCP, the experimental data approached the model values for an interfacial capacitance of 1 mF. However, at applied potentials below OCP, the experimental data were more closely represented by a model using  $C_i = 0.1$  mF. As all of the C<sub>1</sub> values are higher than the normal range of double layer capacitances ( $20 \text{ F/cm}^2$  to  $50 \text{ F/cm}^2$ ), it

is likely that C<sub>i</sub> is composed of a series combination of the double layer and oxide capacitances.<sup>43-44</sup> This capacitance is associated with both double layer and oxide layer. Wren, et al., studied the influence of the oxide film on carbon steel on corrosion rate and C<sub>i</sub> values for three different potential regions: region I ( $\leq -0.6 \text{ V}_{\text{SCE}}$ ), region II ( $-0.5 \text{ V} \leq \text{E}_{\text{SCE}} \leq -0.2 \text{ V}$ ), and region III (0.0 V < E<sub>SCE</sub> < 0.4 V). At different potentials in mildly alkaline solution, a unique value of C<sub>i</sub> was measured. In addition, the oxide films in each of those regions were identified as Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub> layer with Fe<sub>2</sub>O<sub>3</sub>, and FeOOH, respectively. It was concluded that C<sub>i</sub> was related to the composition of the oxide films. Further, it was concluded that the oxide also influenced the nature of the double layer capacitance.<sup>44</sup> Thus, as it relates to the results in this paper, the value of C<sub>i</sub> is likely a combination of double layer capacitance and oxide capacitance. From a model perspective, in order to accurately solve Equation (15) for all DC potentials at 60 Hz, a series of empirical values of capacitance as a function of potential would be needed.

Fitted values of  $C_i$  for each experimental data point in Figure 10 were obtained and the results are shown in Table 2. By using these values along with the other values from Table 1 as input for solving Equation (15), AC(+), AC(-), and AC(avg) were calculated and plotted in Figure 11. Figure 11 is analogous to Figure 6 but for model data only. In addition to these values, the oxidation current passing through  $R_o$  ( $i_o$ ) has also been calculated. This current involves oxidation reactions only and would be analogous to a current calculated from mass loss and Faraday's Law. As in Figure 6, it is seen that AC(avg) from the model was in a good agreement with the oxidation current as described earlier.

## Influence of Frequency and Capacitance on Corrosion Rate with Alternating Current

It is apparent that one of the key parameters in AC corrosion is the value of  $C_i$ . For a given anodic Tafel

Fixed Input Parameters Obtained from Polarization Curve Without AC						
$\beta_a$ (V/decade)	$\beta_{c}$ (V/decade)	$\beta_{H2}$ (V/decade)	i <sub>corr</sub> (A/cm²)	E <sub>corr</sub> (V)	i <sub>l,O2</sub> (A/cm²)	i <sub>0H2</sub> (A/cm <sup>2</sup> )
0.089	0.352	0.205	5.10 <sup>-5</sup>	-0.67	7.10 <sup>-5</sup>	1.10 <sup>-7</sup>

**TABLE 2** 

**TABLE 1** 

	Experimental Data and Input Variables in Solving Equation (15) to Obtain Figures 10 and 11				
E <sub>DC</sub> (V)	RMS (V)	f (Hz)	R <sub>s</sub> (Ω·cm²)	C <sub>i</sub> (μF/cm <sup>2</sup> ) (fitted value)	
-0.74	0.6	60	25	3,500	
-0.72	0.6	60	53	420	
-0.7	0.6	60	53	310	
-0.67	0.6	60	69	261	
-0.6	0.6	60	57	257	
-0.5	0.6	60	54	208	
-0.44	0.6	60	50	309	



**FIGURE 11.** Model Results for 60 Hz AC and 0.6 V RMS for AC(+), AC(-), AC(avg), and  $i_o$  (Equation [15]).

slope, the value of  $C_i$  determines two factors: (1) the magnitude of the Faradaic current at a given frequency and (2) the high-frequency break point at which no Faradaic current is passed. In this section, the response from the model will be explored as a function of AC frequency and  $C_i$ . The model predictions will be compared with results for several cases.

The effect of capacitance on each component of the current for frequencies of 0.01 Hz, 60 Hz, and 1,000 Hz (0.6 V RMS) and an anodic potential of -0.5 V is shown in Table 3. Similar trends were observed at a cathodic potential of -0.7 V. As seen in this table, at both high frequency and low frequency there was little effect of capacitance on the individual components of the current density. For example, the relative magnitudes of each component of current at 0.01 Hz was the same for  $C_i = 0.0001$  F and  $C_i = 0.001$  F. However, at 60 Hz, the difference between the two values of C<sub>i</sub> was dramatic. For example, io at Ci = 0.0001 F was a factor of two as compared to  $C_i = 0.001$  F. This occurs because 60 Hz for this system was close to the high-frequency break point. From a practical standpoint, this finding implies that the growth of an oxide or scale on the surface of the material (owing to a corrosion product or mineral deposition from solution/soil) that alters the interfacial capacitance will greatly impact the AC corrosion rate of the material.

Figure 12 shows model results for the individual components of current in the system at two frequencies in the form of current vs. time data. The data at 60 Hz are presented in Figures 12(a) through (c), where (a) is the oxidation current, (b) is the reduction current, and (c) is the capacitive current. The data at 0.01 Hz are presented in Figures 12(d) through (f), where (d) is the oxidation current, (e) is the reduction current, and (f) is the capacitive current. The data were calculated for the input values from Tables 1 and 3 at OCP. These results show that at 60 Hz most of the current is non-Faradaic, that is, most of the current passes through the interfacial capacitance (Figure 12[c]). Comparison of the oxidation

#### TABLE 3

Effect of Frequency and Capacitance on Faradaic and Non-Faradaic Current at 0.6 V RMS and DC Biases of -0.5 V for  $R_s = 48 \ \Omega \cdot cm^{2(A)}$ 

F (Hz)	C <sub>i</sub> (F)	i <sub>o</sub> (A/cm²)	i <sub>r</sub> (A/cm²)	i <sub>T</sub> (A/cm²)
0.01	0.001	5.3×10 <sup>−3</sup>	$-7.1 \times 10^{-4}$	4.6×10 <sup>−3</sup>
	0.0001	5.3×10 <sup>−3</sup>	$-7.1 \times 10^{-4}$	4.6×10 <sup>−3</sup>
60	0.001	$1.3  imes 10^{-3}$	$-4.2 \times 10^{-5}$	$1.2 \times 10^{-3}$
	0.0001	$4.0  imes 10^{-3}$	$-1.4 \times 10^{-4}$	$3.8 \times 10^{-3}$
1,000	0.001	$1.1 \times 10^{-3}$	$-4.0 \times 10^{-5}$	$1.1 \times 10^{-3}$
	0.0001	$1.1 \times 10^{-3}$	$-4.0 \times 10^{-5}$	$1.1 \times 10^{-3}$

<sup>(A)</sup>Table 1 used as Input values (Equation [15]).

and reduction currents (Figures 12[a] and [b]) shows that the reduction current, which is controlled primarily by the diffusion limited oxygen current density, is negligible relative to the oxidation current. Because the capacitive current sums to zero and  $i_r$  is negligible, the total current is equal to  $i_o$ . This is consistent with the discussion of Figure 6 and is further confirmation that the average current at 60 Hz (AC(avg)) is a good representation of the mass loss of the sample. However, this is limited to DC potentials where the reduction current is controlled primarily by the diffusion limited oxygen current density. In comparison to the 60 Hz data, the waveforms at 0.01 Hz (Figures 12[d] through [f]) are quite different in magnitude and shape. At this frequency the total current is dominated by the Faradaic current  $i_0$  and  $i_r$ , while the  $i_C$  is negligible. From this finding, one would conclude that at this frequency AC(avg) is not a good representation of the mass loss of the sample. This is in agreement with the observation during experiment with AC at lower frequencies (Figure 8).

The total current in the system calculated from the model is compared with the experimental results in Figure 13. In Figure 13, the input values to this model were kept constant (Table 4, the same as Figure 12) for frequencies of 60 Hz and 0.01 Hz. As seen in Figure 13, at these frequencies, there was good agreement in both magnitude and waveform shape between the proposed model and the experimental data. It should be noted that it is not possible to experimentally collect the individual waveforms for the oxidation and capacitive currents presented in Figure 12.

Comparison between the applied potential ( $E_T$ ) at 60 Hz and 0.01 Hz and the corresponding potential across the Faradaic resistance (E) is shown in Figure 14 (parameters from Table 4 as in Figures 12 and 13). The data were generated for an applied potential equal to the OCP, approximately -0.67 V<sub>SCE</sub>, and is shown in each figure. As seen in these figures, for both cases  $E_T$ was higher than E. This is a result of a combination of parameters including the magnitude of the Tafel slopes, the capacitive current in the system, and ohmic drop ( $R_s$ ). These findings reinforce the idea that the potential drop across the system drives the Faradaic reactions in proportion to the anodic and cathodic Tafel slopes;



FIGURE 12. Comparison of the Faradaic and non-Faradaic currents at two different frequencies from the model. At 60 Hz: (a) anodic current, (b) cathodic current, and (c) capacitive current. At 0.01 Hz: (d) anodic current, (e) cathodic current, and (f) capacitive current.



FIGURE 13. Comparison of the total current from the experiment at (b) 60 Hz and (d) 0.01 Hz, and corresponding calculated current from the model ([a] and [c], respectively).



 TABLE 4

 Input Variables for Solving Equation (15) Used to Obtain Figures 12 Through 14

**FIGURE 14.** Comparison of the applied potential at (a) 60 Hz and (b) 0.01 Hz, and corresponding calculated potential across the Faradaic resistance obtained from solving Equation (15) ([c] and [d], respectively).

however,  $E_T$  is not the same as the potential drop across the Faradaic resistances E.

### CONCLUSIONS

Corrosion rates of API grade X65 pipeline steel in sodium chloride solutions with and without 60 Hz AC at different DC potentials were measured using weight loss analysis. These data were compared with the results from a model for AC corrosion that was developed using a modified Butler-Volmer approach. The model considered the anodic and cathodic Tafel slopes, diffusion limited oxygen transport, interfacial capacitance, and solution resistance. Good agreement with the results was demonstrated. From this investigation, it was concluded that:

♦ The presence of an applied AC potential increases corrosion rates at all cathodic and anodic DC potentials between  $-0.725 V_{SCE}$  and  $0.0 V_{SCE}$ , with the

most pronounced increase being at potentials near OCP.

♦ The corrosion rate measured via weight loss agreed most closely with the average AC current passed across the electrochemical interface and not with the average positive AC current. This was shown to be a result of several factors, including a large capacitive current at 60 Hz and a relatively low reduction current limited by oxygen mass transport.

♦ An applied AC potential across an electrochemical interface polarizes the electrode as a function of time away from its DC potential along its polarization curve. The net effect of this polarization depends on a number of variables including: AC frequency, AC potential, Tafel slopes, interfacial capacitance, solution resistance, and applied DC potential.

 $\bigstar \ A \ frequency \ of \ 60 \ Hz \ is \ close \ to \ the \ high-frequency \ breakpoint \ for \ electrochemical \ systems. \ As \ such, \ it \ is \ in \ a \ critical \ frequency \ range \ as \ it \ relates \ to \ corrosion \$ 

rate. Below the high-frequency break point, corrosion rates can vary widely depending on parameters such as interfacial capacitance and solution resistance. Above the high-frequency breakpoint, no change in corrosion rate with AC would be observed.

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#### NOMENCLATURE

i <sub>corr</sub>	Corrosion current density (A/cm <sup>2</sup> )
$E_{corr}$	Corrosion potential (V)
$\beta_{a}$	Anodic Tafel slope (V/decade)
$\beta_{c}$	Cathodic Tafel slope for oxygen reduction
	reaction (V/decade)
E	Potential across the Faradaic resistance (V)
$\mathbf{i}_1$	Oxygen limiting current density (A/cm <sup>2</sup> )
$i_{OH_2}$	Hydrogen exchange current density (A/cm <sup>2</sup> )
$\beta_{H_2}$	Cathodic Tafel slope for hydrogen evolution
-	reaction (V/decade)
R <sub>s</sub>	Solution resistance ( $\Omega \cdot cm^2$ )
Ro	Oxidation resistance ( $\Omega$ )
R <sub>r</sub>	Reduction resistance ( $\Omega$ )
Ci	Interfacial capacity (F/cm <sup>2</sup> )
$i_w$	Current density obtained from mass loss
	$(A/cm^2)$
i <sub>o</sub>	Oxidation current density (A/cm <sup>2</sup> )
i <sub>r</sub>	Reduction current density (A/cm <sup>2</sup> )
$i_{\rm C}$	Capacitive current density (A/cm <sup>2</sup> )
$\mathbf{i}_{\mathrm{T}}$	Total current density passing through the
	system, capacitive + Faradaic (A/cm²)
E <sub>T</sub>	Total applied potential (V)
$E_{DC}$	DC potential (V)
Eo	Peak potential (V)
r	Ratio of anodic to cathodic Tafel slopes
RMS	Root mean square value
AC(+)	Time-averaged positive AC current density
	$(A/cm^2)$
AC(-)	Time-averaged negative AC current density
	$(A/cm^2)$
AC(avg)	Time-averaged AC current density (A/cm <sup>2</sup> )
f	Frequency (Hz)

## APPENDIX A: MATLAB SOLUTION FOR EQUATION (15)

%All electrochemical potentials are vs. SCE.

```
%inputs
                                                                    units
                                                                    \Omega \cdot cm^2 (solution resistance).
    R
    С
                                                                    %F/cm<sup>2</sup> (interfacial capacitance).
                                                                    %A/cm^2 (corrosion current density without AC).
    i corr
    E corr
                                                                    %V (corrosion potential without AC).
                                                                    %V/decade (anodic Tafel slope).
    B_a
    B_c
                                                                    %V/decade (cathodic Tafel slope).
                                                                    %V (DC bias potential).
    E DC
                                                                    %A/cm<sup>2</sup> (oxygen limiting current density).
    i_lim
                                                                    %V (AC potential amplitude).
    E AC
                                                                    %Hz (frequency).
    f
    t0
                                                                    %S (initial time).
    tf
                                                                    %S (final time).
    dt
                                                                    %S.
    ВН
                                                                    %V (Hydrogen Tafel slope).
    i_H
                                                                    %A/cm<sup>2</sup> (Hydrogen exchange current density).
    w=2*pi()*f;
                                                                    %angular frequency.
    tspan=[t0:dt:tf];
%%
%Initial conditions:
%initial current density.
  %i0= -(i_corr*(exp(2.3*(E_DC-E_corr)/B_a)-exp(2.3*(-E_DC+E_corr)/B_c)...
  ./(1-i_corr/i_lim+i_corr/i_lim*exp(2.3*(-E_DC+E_corr)/B_c)))-.....
  i_H*exp(-2.3*(E_DC+0.244)/B_H)). Ref<sup>41</sup>
%initial potential.
  %E0=E DC-i0*R
  E0=E_DC-(i_corr*(exp(2.3*(E_DC-E_corr)/B_a)-exp(2.3*(-E_DC+E_corr)/B_c)...
  ./(1-i_corr/i_lim+i_corr/i_lim*exp(2.3*(-E_DC+E_corr)/B_c)))-.....
  i_H*exp(-2.3*(E_DC+0.244)/B_H))*R;
%%
%equation (15).
  rhs = @(t,E) - E/(C*R)-(i_corr*(exp(2.3*(E-E_corr)/B_a)...)
    -\exp(2.3*(-E+E_corr)/B_c)/(1-i_corr/i_lim+i_corr/i_lim...)
    *exp(2.3*(-E+E_corr)/B_c)))-i_H*exp(-2.3*(E+0.244)/B_H))/C...
    +(E_DC+E_AC*sin(w*t))/(C*R);
  options = odeset('AbsTol', 1e-9, 'RelTol', 1e-9');
  [t,E]=ode23s(rhs,tspan,E0);
%%
%current densities:
ia=i_corr*exp(2.3*(E-E_corr)/B_a);
                                                                    %anodic current density.
ic=(-i_corr*exp(2.3*(-E+E_corr)/B_c)./...
(1-i_corr/i_lim+i_corr/i_lim*exp(2.3*(-E+E_corr)/B_c))...
-i_H*exp(-2.3*(E+0.244)/B_H));
                                                                    %cathodic current density.
dE=diff(E);
dt=diff(t):
dEdt=dE./dt;
i_CC= C*dEdt;
                                                                    %double layer current density.
i=ia+ic:
i_total=i(2:end)+i_CC;
                                                                    %total current density.
ia_avg = trapz(t,ia)/tf;
                                                                    %anodic time averaged current density.
itotal_avg = trapz(t(2:end),i_total)/tf;
                                                                    %total time averaged current density.
```