

Corrosion Rate Estimation from Pseudo-Inductive Electrochemical Impedance Response [☆]

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ABSTRACT

Frequency responses exhibiting pseudo-inductive characteristics have been observed when using the electrochemical impedance technique. Controversy exists in interpreting and modeling such responses to obtain corrosion rates even when linearity between input and output is demonstrated. When the system is poorly characterized, kinetic modeling becomes impossible. Making appropriate use of circuit analogues can be an effective method for estimating the charge-transfer resistance and, thus, the corrosion rate for such a system. This approach is demonstrated for the estimation of the corrosion rate of carbon steel in a poorly characterized waste stream from a chemical plant. The pseudo-inductive characteristics in the frequency response are hypothesized to be caused by an adsorbed intermediate in the corrosion mechanism.

KEY WORDS: corrosion, electrochemical impedance spectroscopy, electrochemical impedance technique, pseudo-inductance, steel.

INTRODUCTION

Pseudo-inductive type of frequency responses have been observed in electrochemical impedance measurements for a number of corroding systems.¹⁻³ Such behavior is characterized by a portion of the impedance spectrum appearing in the fourth quadrant when the data are plotted as the real impedance component versus the negative of the imaginary component. The methods of deducing corrosion rate information from and interpreting this type of response have been somewhat controversial. A portion of this controversy most likely lies in the less than complete understanding of the cause of this type of behavior.

Epelboin, et al.¹ presented the frequency response for iron in 1 molar sulfuric acid with small amounts of propargyl alcohol. This work presented one of the early applications of the electrochemical impedance technique for examining corrosion. These workers claimed that the corrosion rate is correlated with the charge-transfer resistance, "the limit of the faradic impedance at infinite frequency." Later, Lorenz and Mansfeld⁴ and Kendig⁵ showed that this pseudo-inductive behavior was caused by a non-linearity in the frequency response. There is an irreversible desorption of the inhibitor in the vicinity of the corrosion potential.

This non-linearity in the frequency response seems to be caused by the current response to the positive portion of the sine wave voltage excitation being different from the current response to the negative portion of the sine wave voltage excitation. The response of this system was shown to depend on excitation amplitude, exhibiting less pseudo-inductive behavior at lower amplitudes. These observations mean that the possibility of non-linearity between excitation and response must be eliminated before interpreting pseudo-inductive behavior.

Results from several other studies suggest that pseudo-inductive behavior is not necessarily just a result of non-linearity between the perturbation and response. These studies led to at least two interpretations of this type of behavior. Juttner, et al. have shown that such behavior can be simulated by assuming a mechanism derived from bulk diffusion towards a partially blocked electrode surface.⁶ These workers have demonstrated that their partially blocked electrode model can simulate the results for the Ag/Ag⁺ and the Cu/Cu⁺² systems.^{6,7} This approach has promise because it attempts to account for the effect of non-homogeneity of a corroding electrode surface on the frequency response. Such non-homogeneity is one characteristic proposed to cause deviations of the electrode frequency response from so-called ideal behavior modelable by only simple circuit analogues.

The partially blocked electrode theory, while being very promising, is at present difficult to use to simulate the frequency response for systems in which the corrosive medium is ill-defined. The model requires assumptions about the degree of surface blockage, diffusion coefficient, transport layer thickness, and concentrations. Pseudo-inductance in this model is believed to be caused by surface relaxation of the adsorbate. Very often, the needed quantities are difficult or impossible to estimate. As admitted by these workers, further work is required to prove the validity and applicability of the model. Therefore, this theory most likely cannot be used at present to estimate corrosion rates when a pseudo-inductive frequency response is observed in the poorly characterized systems often encountered in real world situations. Implementation of this theory would be difficult on a routine basis.

Another approach to modeling pseudo-inductive frequency responses so as to extract corrosion rate information has been proposed by Armstrong and Henderson⁸ and Epelboin and Keddarn.⁹ Both groups of workers have shown that one model of pseudo-inductive behavior can arise from a corrosion reaction involving an electroactive, adsorbed intermediate. The derivation by

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Gabrielli et al.^{9,10} assumes that the adsorption follows a Langmuir isotherm. Though the derivation is in terms of rate constants, the final equations can be expressed in terms of circuit analogues which model the corrosion process. Armstrong and Henderson showed that circuit analogue based expressions similar to those derived by Gabrielli, et al. could be developed without making any assumptions about the adsorption isotherm. This finding means that the only major assumption that is required to invoke this theory to model a frequency response is that corrosion is caused by an adsorbate reacting with the metal through a two-step charge-transfer reaction with a soluble intermediate adsorbed on the surface. Expressing the model in terms of circuit analogues means that use of the model may not result in fundamental information or understanding because of the difficulties in relating the circuit analogues to a corrosion mechanism. However, corrosion rate information should still be obtainable even in the absence of detailed information about the mechanism. From a practical standpoint, often all that is desired is an estimate of corrosion rate.

Often, the electrochemical impedance technique is used to obtain rapid estimates of corrosion in very poorly characterized systems.¹¹ The corrosion rate itself may be related to either the polarization resistance or the charge-transfer resistance as shown previously.^{10,11} Use of circuit analogues to model the corrosion process offers one reasonable method for obtaining these parameters when little information is available on the solution composition. Use of such circuit analogues to obtain these resistances in the presence of a pseudo-inductive response has been demonstrated by Macdonald¹² who developed a closed form solution to the equations. However, his equations do not account for depression of the capacitive contribution (dispersion of the time constant) when plotted in Nyquist format.

Corroding electrodes often create a frequency response, the capacitive contribution to which is depressed below the real axis when plotted in Nyquist format or the slope is less than 45° on the log(modulus) vs log(frequency) plot. Several explanations have been offered to explain this phenomenon, e.g., cell geometry, surface roughness, reference electrode sensing position, etc.^{13,14} Regardless of the reason for the existence of the depression, the fact that such a deviation from ideal behavior exists means that any model should take account of such depression to enable more accurate estimates of the polarization or charge-transfer resistances to be obtained. The result should be better corrosion-rate estimates for systems whose frequency responses exhibit such behavior.

This type of depression below the real axis may be observed in conjunction with pseudo-inductive behavior. Epelboin and Keddam used a phenomenological time constant raised to a fractional power, $(j\omega\tau_1)^\beta$, $\beta < 1$, to model such data. Such an analysis is borrowed from dielectric relaxation studies.¹³ This approach has already been shown to be practical for analyzing frequency responses having only capacitive contributions.^{11,14} Though this substitution does not result in significant mechanistic information, it does help to model the capacitive portion of the response better than if it were absent. Such inclusion should aid in making better estimates of corrosion rates from electrochemical impedance results.

Recently, studies were undertaken to examine the corrosion of carbon steel in a waste stream from a chemical plant. The electrochemical impedance technique was chosen for the analysis because it offered a method by which corrosion could be estimated rapidly and effects of changes in process variables on corrosion measured rapidly. Some of the frequency responses exhibited pseudo-inductive type of characteristics that were independent of excitation amplitude. Previous results using EMF-pH diagrams suggested that certain components in the waste, most notably iminodiacetic acid, could form complexes with iron under the process conditions.¹⁵ Formation of such a species might affect corrosion. If so, the formation path might proceed through some type of adsorbed intermediate. Such a mechanism might cause the observed pseudo-inductive frequency response.

However, waste streams by their very nature are difficult or impossible to characterize completely. They continuously change. A sample studied in the laboratory is like a "snapshot" of an ever-changing environment. Such streams literally contain all of the unknowns of the chemical plant. However, lack of characterization information does not prevent use of the electrochemical impedance technique for rapid estimation of corrosion rates for one sample caught at one time.

The use of circuit analogues and use of the phenomenological time constant in place of the capacitance allows for either the polarization resistance or the charge-transfer resistance to be estimated even in such a poorly understood system. Thus, this type of modeling bridges the gaps in knowledge so that the electrochemical impedance technique can be used for corrosion rate estimation in complex, poorly characterized systems. This paper provides an example of how analysis using circuit analogues might be used to estimate corrosion rates in the presence of a pseudo-inductive frequency response where little characterization information is available about the environment.

THEORY

Pseudo-inductance may be modeled by the circuit shown in Figure 1. The pseudo-inductance is modeled by a term L similar to that proposed by Macdonald.¹² The capacitance contribution is modeled by the term $(j\omega\tau_1)^\beta/R_t$. This term contains a phenomenological RC time constant τ_1 and an exponent. These terms have been used previously.^{11,14} The exponent β is believed to have little mechanistic information contained in its value since it may account for more than one type of phenomenon. This type of representation of the capacitive contribution when the frequency response also includes a pseudo-inductive contribution has been proposed previously.^{9,11}

The inductance term, L , divided by the faradic resistance, ρ , is a time constant denoted as τ_2 . Substituting τ_2 for L/ρ yields the expression for the frequency response as proposed by Epelboin and Keddam

$$Z = R_s + \left[\frac{1}{R_t} (1 + (j\omega\tau_1)^\beta) + \frac{1}{\rho(1 + j\omega\tau_2)} \right]^{-1} \quad (1)$$

The terms are defined at the end of this paper. This equation was proposed by Epelboin and Keddam⁹ to describe the frequency response of iron in a solution containing 0.1 M sulfuric acid and 0.9 M sodium sulfate. The derivation of Equation (1) assumes that an equilibrium adsorption process with an electron transfer precedes the rate-determining step. Though a Langmuir adsorption isotherm was assumed in the derivation of Equation (1), Armstrong and Henderson⁹ showed that Equation (1) without the phenomenological time constant could be derived without making this assumption about the adsorption process. The time constant and exponent were merely substituted for the capacitance to account for the dispersion as explained by Epelboin and Keddam. The proposal is to use Equation (1) to model the pseudo-inductive frequency response observed for carbon steel exposed to the waste stream environment.

Values for the five variables in Equation (1) should be obtainable by performing a non-linear regression of Equation (1) against the actual frequency-response data. This approach was used by Epelboin and Keddam previously, but their analysis also included the solution resistance.⁹ The present analysis estimated the solution resistance from the high-frequency intercept with the real axis in Nyquist format. Once values of the terms are obtained, the question is how to use them. According to Epelboin and Keddam, R_t should be a charge-transfer resistance and ρ should be a faradic resistance. The charge-transfer resistance has been claimed to be related to the corrosion rate,^{2,10} though one of the bases for this hypothesis was the work using propargyl alcohol, a system for which pseudo-inductance seems to be caused by non-linearity be-

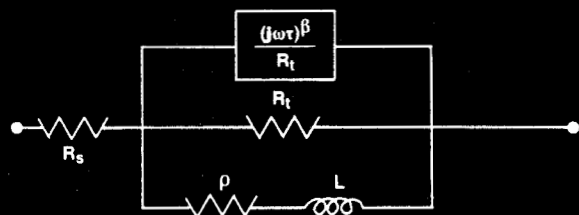


FIGURE 1. Circuit diagram used to model pseudo-inductive electrochemical impedance response.

tween excitation and response that is claimed to result from an irreversible desorption during a portion of the excitation cycle. The hypothesis is that at least in the present study the charge-transfer resistance is the term that can be used to estimate the corrosion rate when pseudo-inductance is observed and when this pseudo-inductance is shown to be independent of excitation voltage amplitude. If so, this quantity may have practical significance for corrosion rate estimation in poorly characterized systems exhibiting pseudo-inductive type of frequency responses.

EXPERIMENTAL

The experimental arrangement has been discussed in detail previously.¹¹ Briefly, a HP⁽¹⁾ 9816S microcomputer guides the experiment by controlling the flow of commands. The frequency response information is measured and calculated by a Solartron⁽²⁾ 1250A frequency response analyzer and a PAR⁽³⁾ 173D potentiostat with 276 programmable interface. The algorithm for the experiment first optimizes the gain of the potentiostat at every half decade of frequency. This optimization is done by finding the maximum gain of the potentiostat that does not cause a current overload. The search is done under computer control. The frequency response curve is then generated. The microcomputer instructs the potentiostat to implement the proper gain at each half decade of frequency. Between 10,000 Hz and 1000 Hz the frequency response curve is generated using the minimum gain (1 ohm). Also, the potentiostat filter is turned on below 0.5 Hz so that only one sine wave is needed at each frequency below that point.

The data are uploaded to an IBM⁽⁴⁾ mainframe computer for analysis in terms of circuit analogues. This program can analyze the results in terms of one of four distinctly different circuits that represent different types of corrosion processes.¹¹ One of these circuits is that shown in Figure 1 to represent Equation (1).

The subroutine used to estimate the circuit elements performs a non-linear regression of the data against Equation (1). The difference is minimized between the sum of the squares of the measured impedance and that calculated from Equation (1). This algorithm is a significant modification of that discussed previously as being used to estimate the parameters needed to model pseudo-inductance.¹¹

The system examined was carbon steel (UNS⁽⁵⁾ G10180) in a combined waste stream from an entire chemical plant. The solutions were made by combining waste solution samples in their "normal" proportions from each of the units in the plant. Water was the predominant component. The exact composition is not known and could not be determined. However, the mixed solution tested is known to have small amounts of iminodiacetic acid, nitrotriacetic acid, low molecular weight organic acids, and ammo-

nium sulfate. The pH was about 7.5. The conductivity was not measured but the small uncompensated resistance estimated from the frequency response and the fairly high ionic content suggest that the waste solution is fairly conductive.

The rotating cylinder electrode used previously¹¹ was also used in this study because of the need to assess if corrosion is sensitive to fluid velocity. All experiments were run under a nitrogen blanket with the nitrogen taken directly from a cylinder. All experiments were run at 48 to 50°C (322 to 323°K) to simulate the upper temperature range for the ambient conditions expected. Two different waste samples retrieved at different times were examined. The rotating cylinder electrode was operated at 200 rpm throughout most of each experiment except for short times at 1000 rpm for velocity sensitivity evaluation. Two of the exposures lasted 24 hours and one lasted about 150 hours. Frequency response curves were generated at several times during each experiment. These curves were generated from 10000 Hz to 0.001 Hz or 0.01 Hz. The excitation signal amplitude was usually 5 mV. Several curves were generated at amplitudes of 2 mV and 10 mV to examine if the excitation and response are independent of amplitude, related linearly.

RESULTS

Figures 2(a) and 2(b) show a typical frequency response curve generated at 5 mV and presented in both Nyquist and Bode format with both the experimental points and the curve calculated from the regression analysis. Table 1 lists the values of the five circuit elements for the three experiments. The first two experiments used the same base stocks to make the combined waste sample. The third data set was generated from carbon steel in a composite waste sample drawn at a different time. Results obtained at both 200 rpm and 1000 rpm are included. Also listed is the amplitude. The agreement in the circuit element values estimated at similar times (e.g., 1 and 4 hours) strongly suggests that the frequency response is independent of excitation amplitude. This finding strongly suggests that the excitation and response are linearly related, at least for amplitudes of 5 mV or less. Figures 3(a) and 3(b) show the frequency response for the same waste sample but generated using an amplitude of 2 mV. The frequency response in Figures 2 and 3 are similar.

Small amplitude polarization curves to ± 20 mV were generated from the corrosion potential after several of the frequency response curves were generated. These curves were used to estimate the polarization resistance as discussed previously.¹¹ The digitized results were curve-fit to Wagner-Traud theory in which one anodic and one cathodic reaction are represented to attempt to estimate the resistance term. The non-linear regression analysis fitted the theory to the data by using adjustable anodic and cathodic Tafel slopes and an adjustable polarization resistance. Since a pseudo-inductive frequency response may be caused by more than one simple anodic and cathodic charge transfer reaction, this procedure may yield inaccurate Tafel slopes and may only provide a rough estimate of the resistance related to the corrosion current.¹⁶ Table 2 shows the resulting resistances. These resistances have not been referred to as polarization resistances for reasons discussed in the next section. Included are the charge-transfer resistances from Table 1 as estimated from Equation (1).

In addition, corrosion rates were estimated from the electrochemical impedance response and measured from the weight change of the immersed samples. The comparison was made for the first two experiments whose duration was 24 hours. The resistance used for the estimation was the average of the values over the 24 hours. The last experiment was run for about 150 hours and the frequency response lost its pseudo-inductive character during the exposure. It ultimately became totally capacitive after 36 to 48 hours and showed two relaxation time constants. This "long-term" frequency response was made able by using a circuit containing two capacitive relaxation time constants.¹¹ Therefore,

(1) Hewlett Packard (HP), Precision Instruments, Palo Alto, CA.

(2) Solartron Instrumentation Group, Sangamo Weston, Inc., Irvine, CA.

(3) EG&G Princeton Applied Research (PAR), Princeton, NJ.

(4) IBM, Armonk, NY.

(5) UNS numbers are listed in the *Metals and Alloys in the Unified Numbering System*, published by the Society of Automotive Engineers and cosponsored by ASTM.

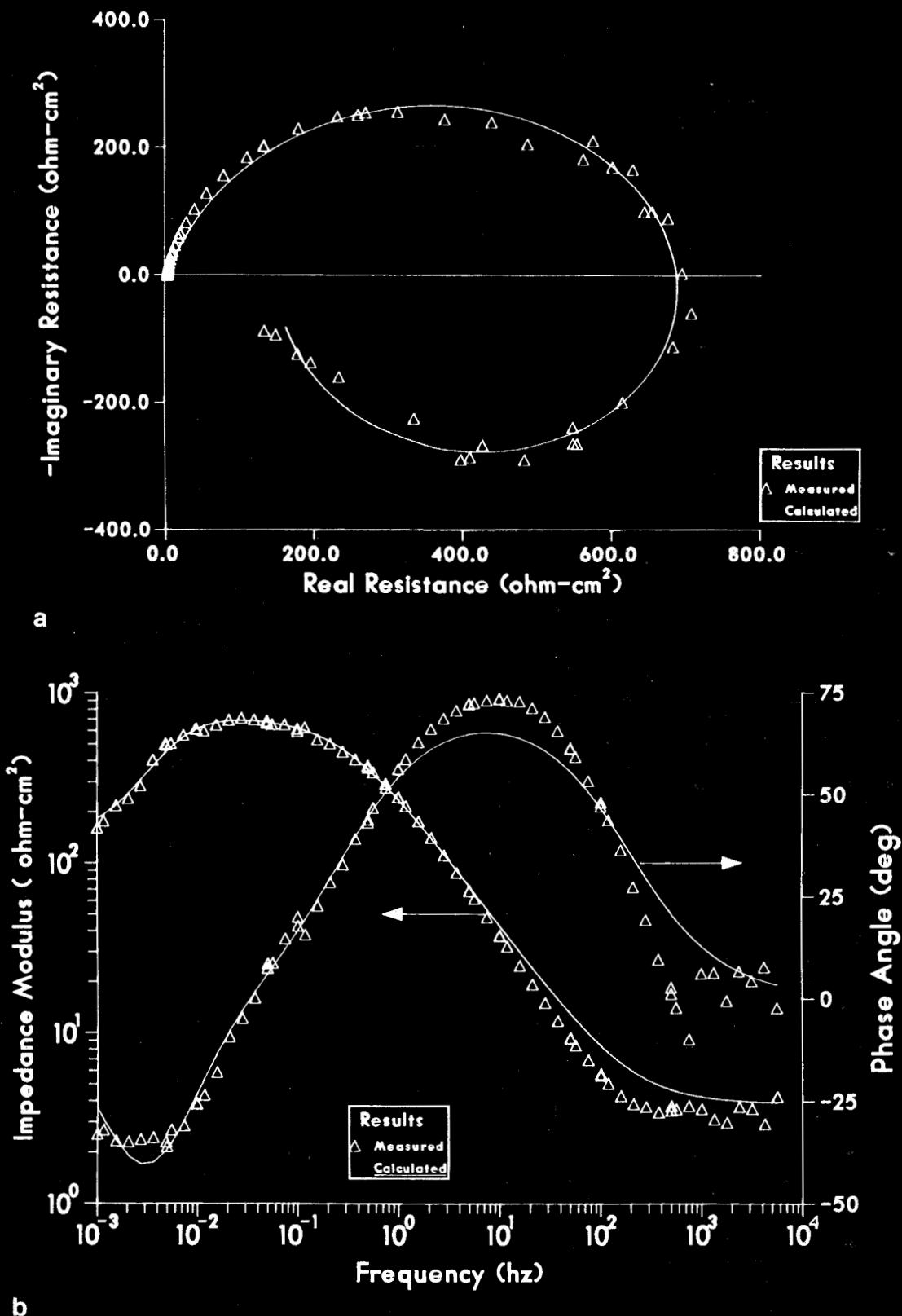


FIGURE 2. Frequency response in (a) Nyquist format and (b) Bode

the mass loss for this sample could not be attributed only to the pseudo-inductive frequency response behavior. Table 3 shows the comparison. A value of 25 mV was assumed for the proportionality constant that relates the charge-transfer resistance to the corro-

sion current. This 25 mV was used instead of values estimated from the DC curve-fitting routine for reasons explained later. Two electrons were assumed to be transferred for each iron atom that reacted.

TABLE 1
Values of Circuit Analogues
that Model Frequency Response

Experiment		Amplitude (mV)	R (ohm-cm ²)	ρ (ohm-cm ²)	β	τ_1 (s)	τ_2 (s)
(rpm)	(h)						
no. 1							
(200)	(0.5)	10	601.	57.	0.85	0.252	150.
(200)	(1)	2	739.	132.	0.79	0.426	77.8
(200)	(4)	5	721.	185.	0.81	0.535	114.
(200)	(24)	5	409.	45.	0.84	0.581	155.
(1000)	(25)	5	198.	3.1	0.86	0.255	651.
no. 2							
(200)	(0.5)	10	538.	13.7	0.87	0.257	768.
(200)	(1)	2	616.	115.	0.80	0.528	194.
(200)	(4)	5	510.	322.	0.83	0.556	80.
(200)	(24)	5	487.	285.	0.85	0.171	50.
(1000)	(25)	5	161.	22.8	0.93	0.062	81.
no. 3 ^(A)							
(200)	(0.5)	5	883.	1.5	0.77	0.274	7300.
(200)	(4)	5	468.	128.	0.70	0.961	92.8
(200)	(24)	5	282.	208.	0.74	1.78	140.

^(A)Experiment no. 3 used a different waste sample and ran for about one week.

DISCUSSION

The results in Figures 2(a) and 2(b) show that Equation (1) can be used to model a pseudo-inductive response in terms of linear circuit analogues. The agreement between the actual data and the calculated curve is reasonable. That the excitation signal and the output impedance are linearly related is supported by the appearance of the same pseudo-inductive behavior being observed when the excitation signal is 2 mV for the same experimental conditions. This similarity is shown in Figures 3(a) and 3(b). The agreement in the figures strongly suggests that the pseudo-inductive type of behavior is not an artifact of excessive amplitude but is caused by certain sub-processes within the overall corrosion mechanism.

Having established that this behavior seems to be caused by the actual corrosion process and that Equation (1) can model the frequency response, the next step is to use the calculated circuit analogues to obtain a corrosion rate estimate. In the Epelboin and Keddam model,⁹ the so-called charge-transfer resistance is related to the current through the Tafel slopes. This resistance term has been called an *infinite frequency charge-transfer resistance* by Armstrong and Henderson.⁸ Gabrielli, et al.¹⁰ refer to this resistance term as the transfer resistance that becomes significant when the current is dependent on two parameters, one being potential and the other being itself dependent on potential and time, e.g., surface coverage. The charge-transfer resistance is the real contribution obtained from the frequency response when this second parameter (e.g., concentration of adsorbed intermediate) cannot follow the perturbation. Its relaxation time constant is far greater than the reciprocal of the perturbation frequency at which the charge transfer process relaxes. This second time constant is a measure of how rapidly this second potential related parameter relaxes to a new value after the potential is changed.¹⁷ Relative values of the time constants shown in Table 1 qualitatively agree with this hypothesis. The relative values suggest that the second sub-process relaxes at a far lower frequency than the first process. In reality, this second parameter could be surface coverage, resistivity of the passive film, etc.¹⁰

In the present analysis, values for the charge-transfer resistances are shown in the first column of Table 1. The hypothesis is that these resistances are related to the corrosion current. They are the appropriate resistances to use to estimate corrosion rates when pseudo-inductive behavior is observed, can be modeled by Equation (1), and such response is not caused by a non-linearity between input excitation and response.

Table 2 shows a comparison between the transfer resistance

from the electrochemical impedance measurement and the resistance estimated by curve-fitting the small amplitude polarization to Wagner-Traud theory in which one anodic and one cathodic reaction are dominant. The agreement between the two resistances is reasonable and suggests that the corrosion current is related to the charge-transfer resistance and not to the zero-frequency polarization resistance for this system.

This agreement in the two resistances is probably related to the similarity between the scan rate used to generate the DC-polarization curve and the effective scan rate as estimated from the frequency at which the capacitive contribution to the frequency response becomes negligible. The DC scan rate was 0.1 mV/s, the lowest scan rate on the PAR 173/276. According to Figures 2(b) and 3(b), the capacitive contribution should be negligible at less than about 0.01 Hz. This frequency corresponds to the point at which the impedance modulus reaches a maximum. Assuming a 5 mV amplitude and the peak reached over one fourth of the sine wave, the 0.01 Hz translates to an effective scan rate of about 0.1 mV/s ($5 \text{ mV} \times \pi/2 \times 0.01 \text{ Hz}$). This agreement suggests that the DC-polarization scan was too rapid to determine the resistance associated with the second relaxation time constant.

The agreement in calculated vs estimated mass loss shown in Table 3 supports the hypothesis that the resistances in Table 2 are related to the corrosion process. The mass losses were estimated from the electrochemical impedance response by assuming a constant of 25 mV to relate the charge-transfer resistance to the corrosion current. The resistances were averaged over the entire experiment but only for constant rotation rate. This value of 25 mV was used in lieu of an accurate estimate for the Tafel slopes.

This proposal that the charge-transfer resistance relates the Tafel slopes to the corrosion current for a system in which an adsorbed intermediate is present has been advanced before by Gabrielli, et al.¹⁰ for the iron-sulfuric acid system. In that case, the proposal was that the faradic impedance is related to the sum of the Stern-Geary relationship and a term dependent on surface coverage. The Stern-Geary relationship was proposed to include the charge-transfer resistance and not the polarization resistance. If that proposal also applies to this system, then the corrosion rate here is related to the charge-transfer resistance, which in turn is estimated by R_t in Equation (1). Results in Tables 2 and 3 support this conclusion. This conclusion is hypothetical because the complexity of the waste stream prevented significant characterization to be made of the contents and more definitive kinetic equations to be derived.

One potential error in the comparison shown in Table 2 arises from the question of the validity of the analysis using

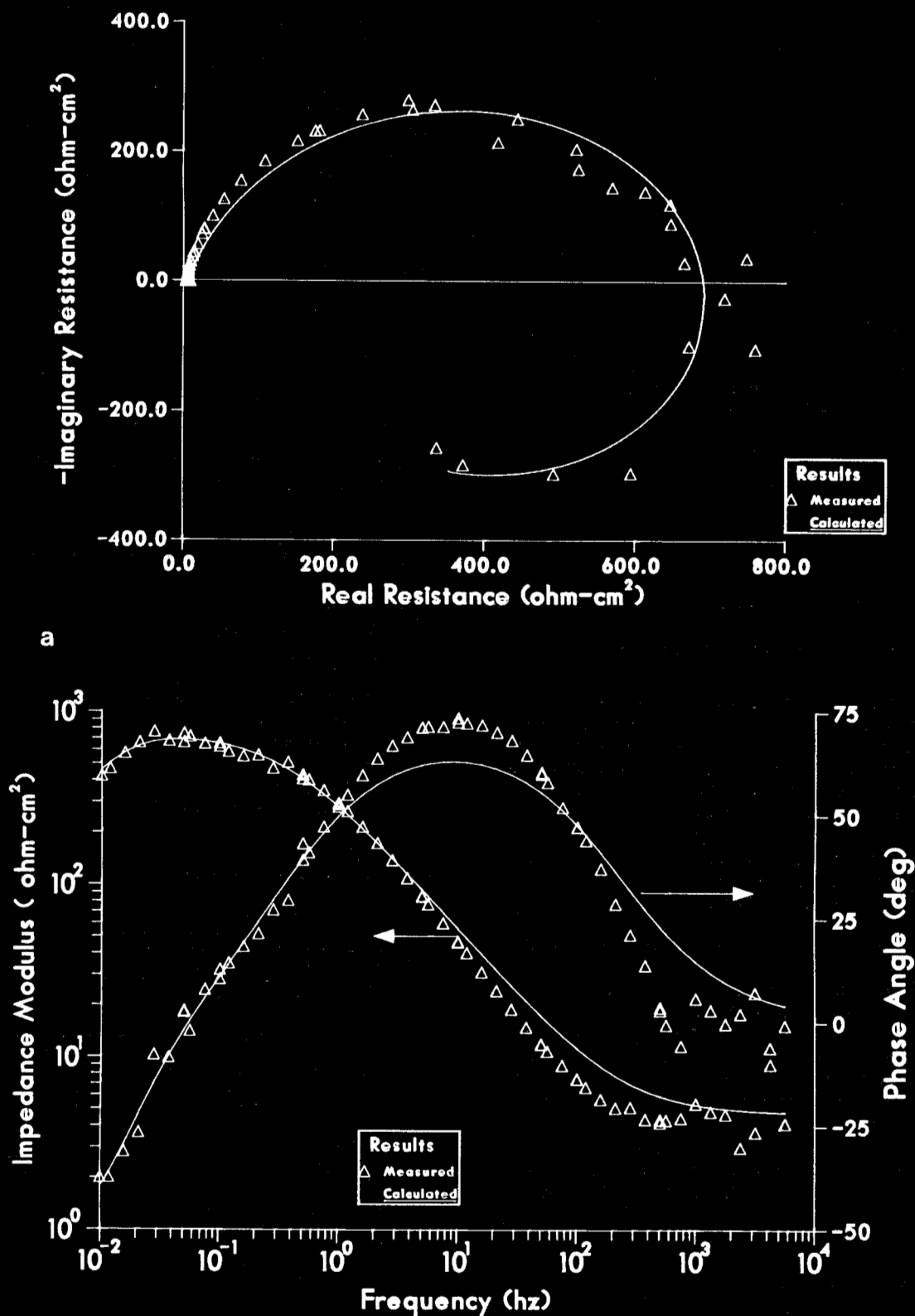


FIGURE 3. Frequency response in (a) Nyquist format and (b) Bode format of carbon steel in same environment as Figure 2 but with 2 mV amplitude excitation and after 1 hour of exposure.

Wagner-Traud theory with only two exponential terms, one for an anodic and one for a cathodic reaction, to model the DC-polarization response. If the cause of the pseudo-inductive behavior is a corrosion mechanism in which an adsorption equilibrium precedes

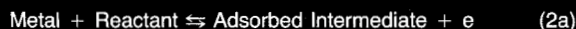
the rate determining step, then this analysis may be approximate because more than two charge transfer reactions may be impacting the rate. This scheme is shown conceptually in Equations (2a) and (2b),

TABLE 2
Comparison of Resistances from
AC vs DC Type Measurements

Experiment (h)	Impedance R_t (ohm-cm ²)	DC Polarization R_t (ohm-cm ²)
no. 1 (4) (24)	721. 409.	490. 305.
no. 2 (4) (24)	510. 487.	436. 410.
no. 3 (24)	282.	227.

TABLE 3
Estimated vs Measured Corrosion Rates

Experiment	Corrosion Rate	
	Impedance mm/y (mpy)	Measured mm/y (mpy)
no. 1	0.51 (20)	0.74 (29)
no. 2	0.56 (22)	0.71 (28)



However, if application of a DC voltage does not greatly disturb the equilibrium of Reaction (2a), then Reaction (2b) should remain the rate-controlling reaction. Then, only one anodic Reaction (2b) and one other cathodic reaction, e.g. hydrogen ion reduction, may become important. Use of two exponential terms may model the response reasonably well under these circumstances.¹⁶

Previously,¹⁵ iminodiacetic acid (IDA) was suggested to be the species that could be accelerating corrosion. Thermodynamic, EMF-pH diagrams supported this suggestion. If so, two possible reactions with IDA could be contributing to the corrosion reaction. These reactions would result in the formation of Fe(IDA) or Fe(IDA)₂⁻². Thermodynamically, the most stable form is Fe(IDA)₂⁻² at the pH, temperature, corrosion potential, and concentration in the waste stream.¹⁵ The formation of this species by reaction of Fe with IDAH⁻, the stable form of IDA at a pH of 8, is $-0.78 V_{\text{SHE}}$. The corrosion potential is about $-0.4 V_{\text{SHE}}$. This large difference in potential suggests that an absorption equilibrium like Equation (2a) may be hardly affected by an additional 20 mV polarization around the corrosion potential if IDA is, indeed, the adsorbing species.

If the individual charge transfer reactions in Equilibrium (2a) are each hardly affected by the small voltage perturbation at the effective frequency of the 20 mV polarization scan, then Reaction (2b) may be the only major anodic contributor to the corrosion current when the offset from the corrosion potential is small (± 20 mV) and the scan rate is faster than the relaxation process of Reaction (1). If so, Equation (2b) might be considered to be the dominant anodic charge transfer reaction. Then, estimation of the resistance from DC measurements made by using only two exponentials, one each for the anodic and cathodic reactions may be a reasonable approximation. Of course, this entire discussion is

predicated on IDA being the adsorbing species that affects the corrosion rate. Characterization of the iron-waste interaction could not be done to confirm this assumption. However, the agreement in Table 3 between corrosion rates estimated from mass loss and from the model strongly suggests that the pseudo-inductive characteristics of the frequency response are caused by the corrosion process itself.

Accurate Tafel slopes are difficult to obtain by non-linear regression when including the exponential terms as exponentials. Linearization of these terms by expansion into a power series might have been helpful.¹⁸ However, no attempt was made to write a program to adopt this procedure for this analysis. Therefore, 25 mV was assumed as the proportionality between the corrosion current and resistance for the determination of the mass loss. As shown by the agreement in Table 3, the 25 mV estimate is adequate in this case.

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LIST OF SYMBOLS

- $j = \sqrt{-1}$
 $L =$ inductance (henry)
 $R_s =$ solution resistance (ohm-cm²)
 $R_t =$ charge-transfer resistance (ohm-cm²)
 $Z =$ impedance (ohm-cm²)
 $\beta =$ phenomenological exponent (dimensionless)
 $\rho =$ faradic resistance (ohm-cm²)
 $\tau_1 =$ capacitive time constant (s)
 $\tau_2 =$ inductive time constant (s)
 $\omega =$ frequency (radians-s⁻¹)
 $(\omega = 2\pi f \text{ where } f \text{ is in Hertz})$

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