



AC IMPEDANCE STUDIES ON THE CORROSION BEHAVIOR OF CARBON STEEL IN DEAERATED CHLORIDE SOLUTION

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ABSTRACT

In many engineering applications such as desalination process, an option for corrosion control is oxygen removal, but there is little experimental data regarding corrosion rates in such environments.

Electrochemical impedance spectroscopy (EIS) has been used for the study of the behavior of corroding metals and data interpretation is often accomplished by means of electronic equivalent circuits. Such circuits can be used to ascertain various corrosion related phenomena and thus the corrosion characteristics of the system are evaluated. Electrochemical impedance spectra have been obtained at the corrosion potential for carbon steel rotating cylinder electrode (RCE) in deaerated 1 M NaCl solutions at 50° C at different pH's. In addition, dc measurements were also carried out which show a significant effect of rotation speed of the RCE on the cathodic reaction at pH 4 and thereby, giving evidence that the corrosion rate is diffusion controlled. As pH increases, the effect of rotation speed on the corrosion rate decreases. Analysis of the impedance measurements shows that one time constant in an impedance spectrum has been generated at pH 4 whereas two times constant was generated at pH 9.5.

Keywords: *carbon steel, deaeration, ac impedance, chloride solution, rotating cylinder*

1. INTRODUCTION

Multi Stage Flash evaporation (MSF) is the main process used for production of desalinated water in SWCC's seawater desalination plants. Carbon steel and wide variety of materials are used in MSF plants. These plants offer numerous corrosion problems due to process conditions. To reduce the corrosion rates, removal of oxygen from the seawater by physical and chemical methods is used. Therefore, mechanistic studies are required, which can provide experimental data to have good understanding of the corrosion behavior of metallic materials in these environments. Some studies involving the use of a range of materials have been carried out under actual service conditions in desalination plants [Hodgkiess et al, 1983, Wood, F. C. and Y. N. Wu, 1979, Harding, K. and D.A. Bridle, 1979, Schrieber et al, 1976, Heitz, E. and R. Manner, 1978] and in laboratory conditions [Sakuma et al, 1974, Hodgkiess et al, 1979] using aerated and deaerated seawater at temperatures up to 90°C and within different pH range.

The corrosion of carbon steel in chloride containing solutions is known to be due to the presence of dissolved oxygen but the effect of deoxygenation on both the dc and ac electrochemical responses has not been widely discussed. The reduction in corrosion rate due to the deaeration is well known [Ismaeel A. and S. Turgoose, 1999] and is the basis of the cathodic action but the effect of velocity under different pH's at deaeration condition has not been given much attention.

The electrochemical impedance technique is a well established method for the investigation of electrochemical reactions. However, the analysis of the resultant data remains difficult. The most common approach is based on the equivalent circuit concept, exemplified by the model of Randles [Randles, J. E. B., 1947]. This study is concerned with the electrochemical measurements, both dc and ac measurements, of carbon steel corrosion in deaerated 1 M NaCl solution at 50°C and the effect of rotating cylinder speed under different pH's.

2. EXPERIMENTAL DESIGN

Specimens used in the electrochemical measurements were machined from carbon steel rod. The shape of the specimen was cylindrical, 0.8 cm long and 1.2 cm in diameter with a central cylindrical hole to fit on the stainless steel shaft, which rotates the specimen. The rotating cylinder equipment is schematically shown in Figure 1. Above the specimen the shaft was fixed in a long Teflon cylinder and below the specimen Teflon cap was screwed on to hold the specimen tightly. The diameter of the specimen was exactly the same as that of the upper Teflon coated shaft or lower Teflon cap. Thus the specimen became a part of the long cylinder exposing the peripheral surface of the specimen to the test solution. The surface of each specimen was carefully polished with 600-grit silicon carbide paper to obtain uniform results.

The samples were rotated with EG&G rotating cylinder equipment model 616, which enables the rotation speed to be varied from 1 to 9999 rpm.

3. METHODOLOGY

The specimens were prepared by polishing on 600 grit silicon carbide paper, then rinsed with distilled water and finally dried in a stream of air. The corrosive media were 1.0 M NaCl. The pH of solution was adjusted to different range values from pH 4 to pH 9.5 by adding dilute HCl and NaOH solutions. To scavenge the dissolved oxygen, test solution was heated to 50°C and then Na₂SO₃ was added. N₂ gas was constantly purged to maintain the deaerated condition. The carbon steel electrode was immersed in the sealed cell containing the test solution. A saturated calomel electrode and platinum electrode was used as reference and counter electrodes, respectively. After 1 hour, when a constant potential was attained, ac and dc measurements were carried out. The readings were taken at rotation speed of 0, 2000, 3000 and 5000 rpm under different pH's.

The slope, $\Delta E/\Delta I$, at the corrosion potential, is defined as polarization resistance, R_p . If we define the constant B as:

$$B = b_a b_c / 2.3(b_a + b_c)$$

Where b_a and b_c are the Tafel slopes determined from the E vs. $\log_{10} I$ plot.

The corrosion current density is given by:

$$I_{\text{corr}} = B / R_p$$

The potentiodynamic polarization measurements were carried out using a scan rate of 0.1 mV/s in the range of -250 mV to + 250 mV vs. free corrosion potential. The electrochemical impedance measurement were performed under potentiostatic conditions at the corrosion potential by means of a frequency response analyzer, Solartron 1250, and 1287 Electrochemical interface using small amplitude sine wave signals, 10 mV, over the frequency range of 1 kHz to 1 mHz, with 5 points per decade. This technique is based on the theory that describes the response of a circuit to an alternating current or voltage as a function of frequency.

4. EXPERIMENTAL RESULTS

4.1 DC measurements

The corrosion behavior of carbon steel has been studied under dynamic condition by rotating cylinder electrode (RCE) at rotation speed of 0, 500, 1000, 2000 and 3000 rpm, in deaerated 1.0 M NaCl solution at 50°C and different pH's.

The corrosion rates of carbon steel in deaerated 1.0 M NaCl at pH 4 are shown in Table 1.

Table 1 Corrosion rates of carbon steel in deaerated 1.0 M NaCl at 50°C and pH 4 under static conditions and at different rotation speed

RPM	0	500	1000	2000	3000
$I_{\text{corr}}, \mu\text{A}/\text{cm}^2$	43	157	265	280	280
C.R , mpy	20	73	123	130	130
E_{corr} , mV	-736	-719	-708	-700	-700

The results indicate that the corrosion rate of carbon steel increased from 20 mpy at static condition to 130 mpy at velocity of 2000 rpm. E_{corr} values become more positive with increase in rotation speed of the electrode. As the velocity is increased further (3000 rpm) the corrosion rate and corrosion potential do not change.

The potentiodynamic polarization curves of carbon steel at pH 4 in deaerated 1.0 M NaCl solution at 50°C and rotation speed of 0, 500, 1000, 2000 and 3000 rpm are shown in Fig. 2. It can be seen from Fig. 2 that limiting diffusion current density increases with increasing rotation speed. Higher values of corrosion current and corrosion potential are also recorded with increase in rotation speed.

It is apparent that the change in the rotation speed influences the corrosion behavior of carbon steel. However, as rotation speed is increased from 2000 to 3000 rpm, the corrosion rate remains constant at 130 mpy. Corrosion rate becomes independent of velocity at very high speed, which mean that the reduction reaction becomes activation-controlled. Since velocity has no effect on activation-controlled systems this explains why does the polarization curve at 3000 rpm in Fig. (2) overlap with the polarization curve at 2000 rpm. Graphically it can be illustrated by the Evans diagram as shown in Fig. 3.

The cathodic limiting current density, i_L , can be calculated from the equation:

$$i_L = \frac{DnFC_b}{d}$$

Where i_L is the limiting diffusion current density, D is the diffusion coefficient of the reacting ions, (H^+), C_b is the H^+ concentration of the uniform bulk solution, and d is the thickness of the diffusion layer. Thus, i_L is increased by higher solution concentration, C_b ; higher temperature, which increases D ; and higher solution agitation, which reduces d .

Mass transfer coefficient, $K = \frac{D}{d}$

In turbulent flow for RCE geometry:

$$K = \frac{D}{d} 0.079 \left(\frac{ud}{\nu} \right)^{0.7} \left(\frac{\nu}{D} \right)^{0.356}$$

Where:

$$\left(\frac{ud}{\nu} \right): \text{Reynolds No. and } \left(\frac{\nu}{D} \right): \text{Schmidt No.}$$

As velocity, u , increases mass transfer coefficient, k , increases and corrosion current increase

At pH 6, the corrosion rates of carbon steel in deaerated 1.0 M NaCl at 50°C and at different rotation speeds are tabulated in table 2.

Table 2 Corrosion rates of carbon steel in deaerated 1.0 M NaCl at 50°C and pH 6 under static conditions and rotation speeds of 1000, 2000 and 3000 rpm.

RPM	0	1000	2000	3000
I_{corr} , $\mu\text{A}/\text{cm}^2$	10	24	31	31
C.R , mpy	4.6	11	14.7	14.7
E_{corr} , mV	-768	-748	-742	-742

The results at pH 6 show that the corrosion rates of carbon steel increases as the rotation speed increases and E_{corr} values becomes more positive with increase in rotation speed of the electrode.

The potentiodynamic polarization curves of carbon steel at pH 6 in deaerated 1.0 M NaCl solution at 50°C and rotation speed of 0, 1000, 2000 and 3000 rpm are shown in Fig. (4).

At pH 9, the corrosion rate results of carbon steel in deaerated 1.0 M NaCl at 50°C under static and rotation speed of 2000 and 3000 rpm are tabulated in table 3.

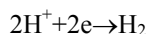
Table 3. Corrosion rates of carbon steel in deaerated 1.0 M NaCl at 50°C and pH 9 under static conditions and rotation speed of 2000 and 3000 rpm.

RPM	0	2000	3000
I_{corr} , $\mu\text{A}/\text{cm}^2$	3.8	5	5
C.R , mpy	1.7	2.3	2.3
E_{corr} , mV	-804	-798	-798
b_C , mV/decade	197	169	169

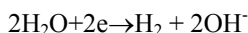
The potentiodynamic polarization curves of carbon steel at pH 9 in deaerated 1.0 M NaCl solution at 50°C and under static and rotation speed of 2000 rpm are shown in Fig. (5). The results indicate that at pH 4, the effect of solution speed on corrosion rate is more pronounced and corrosion rate increases almost linearly. The corrosion rate at 2000 rpm is about 6 times

more than that under static condition. At pH 6 and 9, the effect of solution speed on corrosion rate is less pronounced. At pH 6 the corrosion rate at 2000 rpm is 3 times more than that under static condition whereas at pH 9 the increase is less than 1.5 times. Hence, in deaerated solution the corrosion rates of carbon steel greatly depend on flow rate as the pH is lowered from 9 to 4.

From E-pH diagram (Pourbaix) of iron it is notable that the difference between the stability line for water and iron decreases significantly as pH increases. At low pH, the H^+ will first be consumed by this reaction:



Until the pH increases sufficiently that water is decomposed directly to hydrogen by:



At pH 4, the equilibrium potential of hydrogen, (E_{H^+/H_2}), is more noble than at pH 9 ($E_{H^+/H_2} = 0 - 0.059 \text{ pH}$) and the exchange current density, I_{0H^+/H_2} shifts to higher value than at pH 9. Hence, the difference between E_{H^+/H_2} and $E_{Fe^{2+}/Fe}$ is small at high pH and large at low pH. Thus, at low pH the corrosion rate is diffusion controlled, while the iron oxidation curve will intersect the cathodic reaction curve at the limiting current region where increasing the velocity or agitation of the corrosive medium will increase corrosion rate. At high pH the corrosion rate is activation controlled, while the iron oxidation curve will intersect the cathodic reaction curve at near activation region where the corrosion is controlled by the reaction sequence at the metal-electrolyte interface, agitation will have no influence on corrosion rate. Figure 6 shows the comparison in potentiodynamic polarization curves of carbon steel in deaerated solution at different pH. It shows that a passive film is formed on the steel surface at pH 9.5.

4.2 AC measurements

Figure 7 shows the Nyquist and Bode plots of the carbon steel in deaerated 1.0 M NaCl at 50°C and pH 4 at static condition and rotation speed range of 1000 to 5000 rpm.

Nyquist plot made by plotting the imaginary impedance component (Z'') against the real component (Z') at each excitation frequency. Frequency is increasing in a counterclockwise direction. At high frequencies, the impedance is almost entirely created by the solution resistance, R_s . At the low frequencies, the impedance is almost entirely created by the combined polarization resistance and solution resistance. Thus, R_p is the difference between the low frequency limit and the high frequency limit. It is apparent that the change in the rotation speed influences the diameter length of the semicircles, R_p .

The $|Z|$ vs. f plot also yield values of R_s and R_p . While R_s is the high frequency limiting value of $|Z|$, the R_p is the difference between the low frequency limit and the high frequency limit. No effect on R_s observed with increasing rotation speed. This behavior is in agreement with the dc results, which indicate that the corrosion reaction is strongly controlled by diffusion through a fluid boundary layer.

Figure 8 shows the Nyquist and Bode plots of the carbon steel in deaerated 1.0 M NaCl at 50°C and pH 9.5. The comparison in ac spectrum between pH 4 and pH 9.5 are shown in Figure 9.

4.2.1 Fitting data

Figure (10) shows fitting results at pH 4 under static condition. Values of the components are listed with the relative error. R_s fitted value was 0.855 Ohm.cm² with ± 0.020 error. Double layer capacitance is replaced by a constant phase element, CPE. Charge transfer resistance was 237.5 with ± 4.1 error. Chi-Squared was 0.01318, which is the square of the standard deviation between the original data and calculated spectrum. Weight sum of squares was 1.476, which is proportional to the average percentage error between the original data points and the calculated values. Fitting lines are nearly matching Bode and Nyquist curves indicating that the best fit equivalent circuit at pH 4 are the parallel combination of the charge transfer resistance of the metal and double layer capacitance with one relaxation time constant.

Potentiodynamic polarization results at pH 9.5 as mention in the dc measurements show that a passive film is formed on the steel surface and the corrosion rate was activation controlled.

Analysis of the impedance spectrum, through fitting results (Figure11), shows that the equivalent circuit at pH 9.5 give better fit consisting of two circuits. A parallel combination of capacitance with resistance as a series to the circuit of cathodic branch as a charge transfer resistance with parallel charge transfer resistance-diffusional impedance for the anodic branch. The circuit after solution resistance is attributed to the passive film, which formed on the metal surface. Thus, the spectrum is resolved into two times constant.

5. CONCLUSIONS

The corrosion behavior of carbon steel in deaerated 1 M NaCl solution was studied by ac and dc measurements which gives good understanding of under going corrosion processes. The effect of velocity on the corrosion behavior of carbon steel, by dc measurements, is pH dependent; while the corrosion rates are greatly influenced by rotation speed at pH 4 but the effect of velocity on the corrosion rate decreases as pH increases. This is attributed to the fact that at pH 4 the corrosion rate is diffusion controlled, where reduction of H^+ is dominant reaction. At higher pH solution, $[H^+]$ becomes much lower, and therefore reduction of H_2O is predominant and corrosion rate is activation controlled. Analysis of the impedance spectrum

shows that one time constant in an impedance spectrum has been generated at pH 4 whereas two times constant was generated at pH 9.5.

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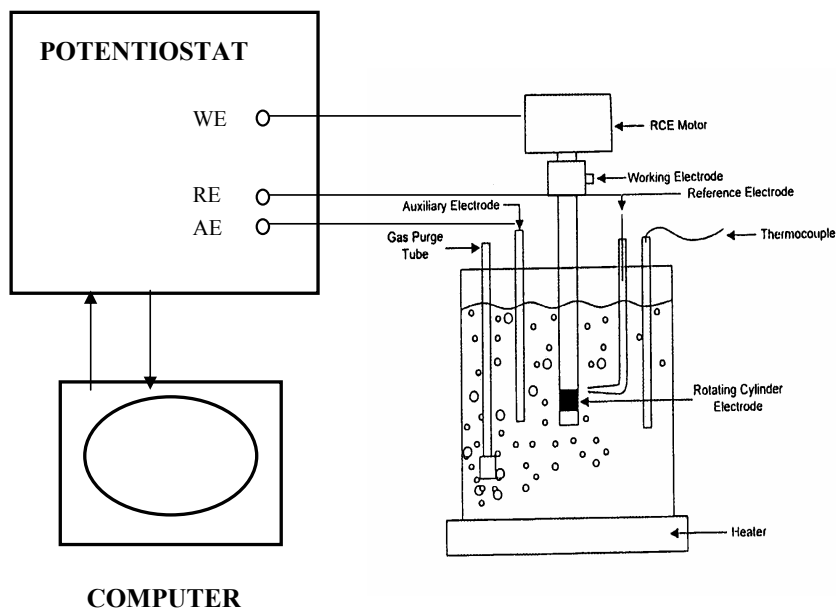


Figure 1. A schematic diagram of the experimental set up

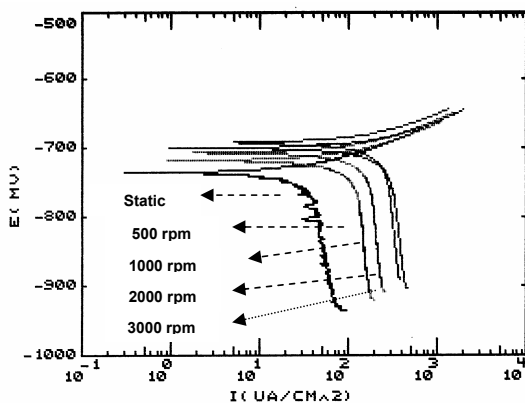


Figure 2. Potentiodynamic polarization curves for carbon steel in deaerated 1.0 M NaCl solution at 50°C and pH 4 under dynamic condition

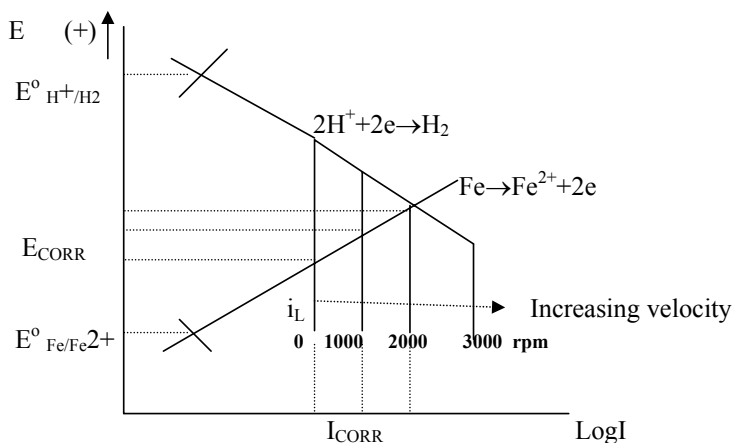


Figure 3. Evans diagram for difference rotation speed for carbon steel in deaerated 1.0 M NaCl solution at 50°C and pH 4.

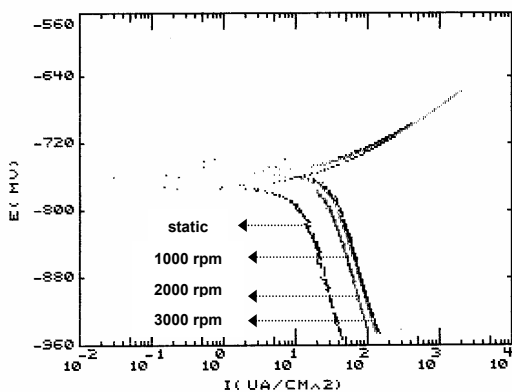


Figure 4. Potentiodynamic polarization curves for carbon steel in deaerated 1.0 M NaCl solution at 50 °C and pH 6 under static and dynamic condition

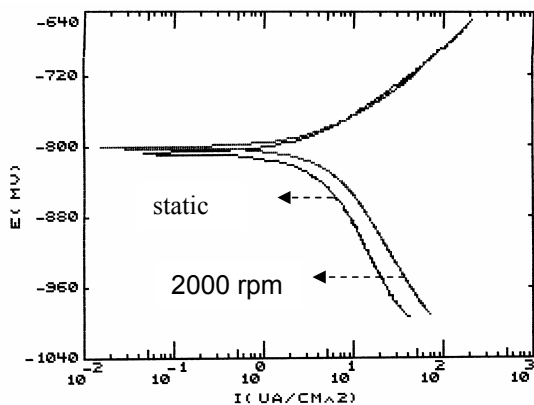


Figure 5. Potentiodynamic polarization curves for carbon steel in deaerated 1.0 M NaCl solution at 50 °C and pH 9 under static and dynamic conditions

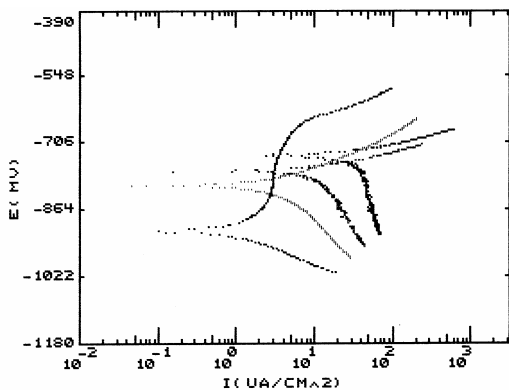


Figure 6. Potentiodynamic polarization curves of carbon steel in deaerated 1.0 M NaCl solution at 50° C and different pH

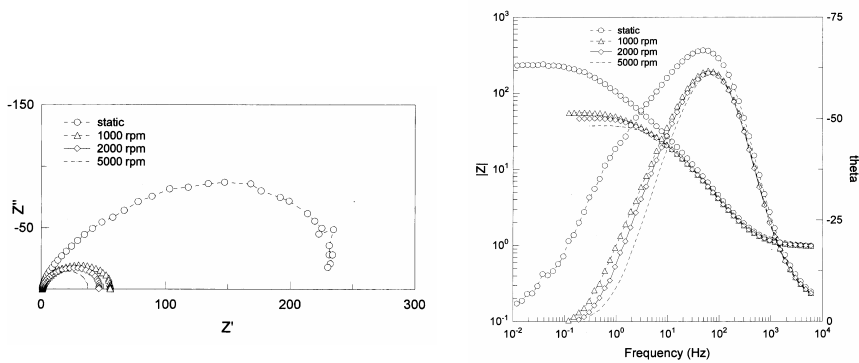


Figure 7. AC spectrum for carbon steel in deaerated 1 M NaCl at 50°C and pH 4

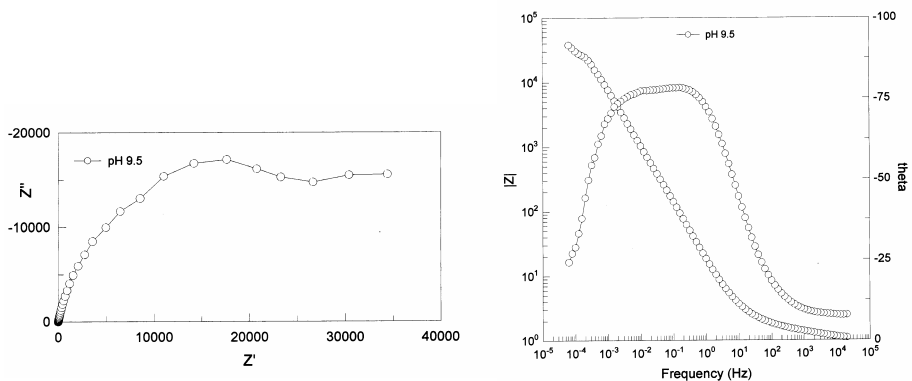


Figure 8. AC spectrum for carbon steel in deaerated 1 M NaCl at 50°C and pH 9.5.

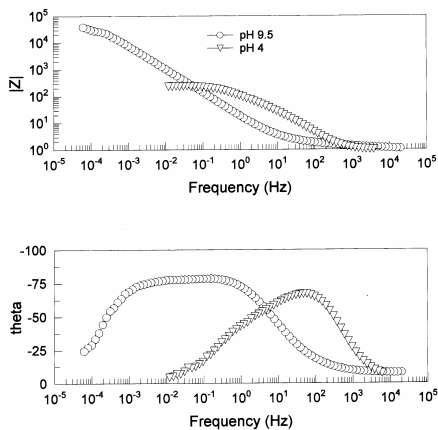
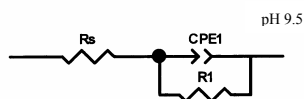
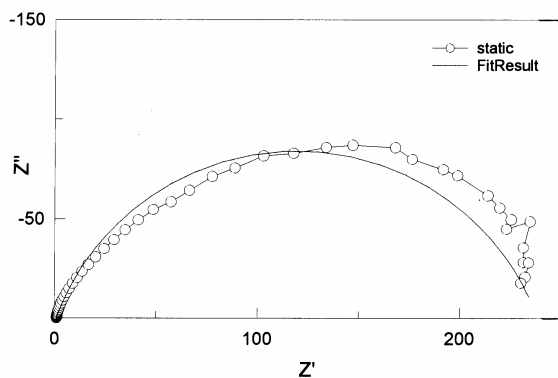
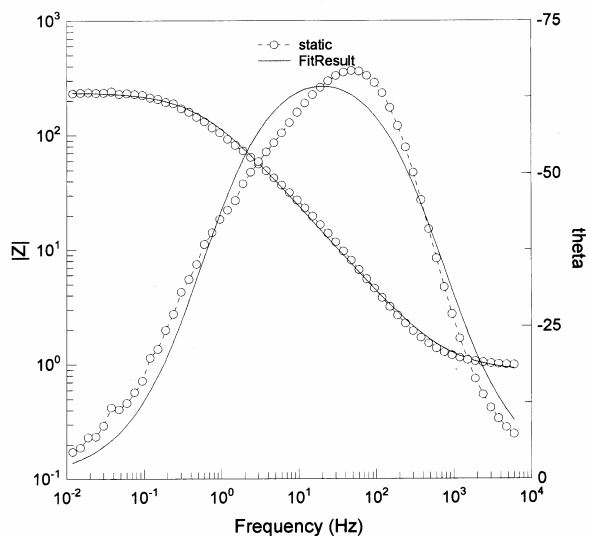
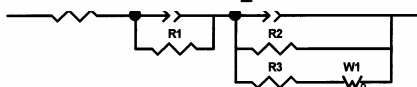
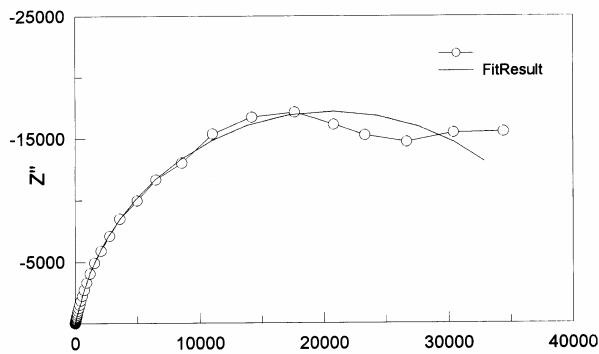
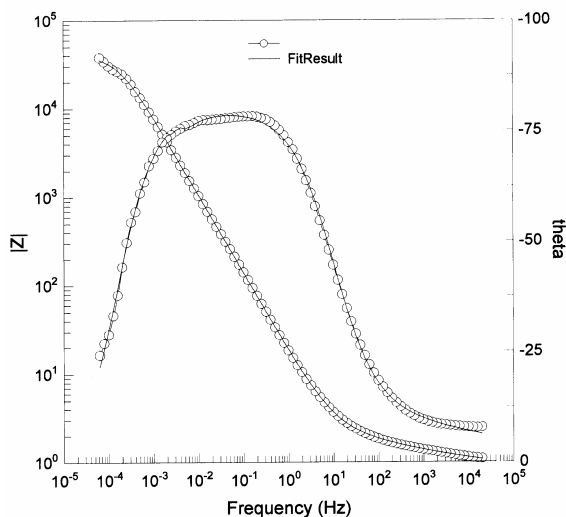


Figure 9. Comparison in ac spectrum between pH 4 and pH 9.5 for carbon steel in deaerated 1 M NaCl at 50°C



Element	Freedom	Value	Error	Error %
Rs	Free(+)	0.85538	0.020863	2.439
CPE1-T	Free(+)	0.0015878	4.5809E-5	2.8851
CPE1-P	Free(+)	0.78374	0.0054793	0.69912
R1	Free(+)	237.5	4.1634	1.753
Chi-Squared:		0.013182		
Weighted Sum of Squares:		1.4763		

Figure 10. Fitting results for carbon steel in deaerated 1 M NaCl at 50°C and pH 4 at static condition



Element	Freedom	Value	Error	Error %
Rs	Free(+)	0.7492	0.056037	7.4796
CPE1-T	Free(+)	0.15445	0.033251	21.529
CPE1-P	Free(+)	0.24453	0.030008	12.272
R1	Free(+)	3.704	0.98274	26.532
CPE2-T	Free(+)	0.011101	4.4344E-5	0.39946
CPE2-P	Free(+)	0.88707	0.0011192	0.12617
R2	Free(+)	42940	1104.2	2.5715
R3	Free(+)	49287	12474	25.309
W1-R	Free(+)	9.4127E5	5.055E5	53.704
W1-T	Free(+)	69.87	0.90972	1.302
W1-P	Free(+)	4.935	0.048481	0.98239

Chi-Squared: 0.00088712
 Weighted Sum of Squares: 0.14283

Figure 11. Fitting results for carbon steel in deaerated 1 M NaCl at pH 9.5 and 50°C under static condition