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EFFECT OF RADIO FREQUENCY TREATMENT OF WATER ON SCALE
FORMATION AND CORROSION

A Thesis
Presented for the
Master of Science
Degree

The University of Tennessee, Knoxville

Venkata R. Kodali
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ABSTRACT

The effects of radio frequency treatment of water on scale formation and corrosion were studied. Mass-loss measurements, microscopic surface examinations, and electrochemical impedance spectroscopy were used to evaluate the scale formation rates and corrosion rates of carbon steel specimens exposed to a supersaturated calcium carbonate solution (test medium) under radio frequency (RF) treated and untreated conditions. For comparison, specimens were also exposed to untreated tap water. The results are summarized as follows. In the untreated test medium, a thick, porous scale layer was formed. In the RF treated test medium, a thinner, more porous scale layer was formed. Also, a time lag was associated with scale formation in the RF treated medium. The carbon steel exhibited the lowest corrosion rate in the untreated test medium, the highest corrosion rate in the untreated tap water (no scale), and an intermediate corrosion rate in the RF treated test medium. It was concluded that the RF treatment slowed down the rate of scale formation and modified the scale characteristics. It was also concluded that the RF treatment did not affect the basic corrosion mechanism, but rather influenced the corrosion rate by changing the scale characteristics and therefore the corrosion protection associated with the scale.

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CHAPTER I

INTRODUCTION

The formation of deposits by insoluble salts in boilers, cooling water systems, hot water heaters, and water distribution lines has been known for a long time. On a daily basis, these deposits are seen on the waterside surfaces of tea kettles and coffee makers. These deposits are often classified as: (1) scales -- firm, hard, dense, adherent deposits of mineral particles, (2) incrustations -- deposits that are more or less firmly adherent to the metallic surface, or (3) sludges -- deposits that are loose precipitates, less adherent and more permeable than scales and easily removed by mechanical means.

The formation of scale on the waterside surfaces of various heat transfer systems has been a matter of great concern in many industries over the years. The presence of scale on heat transfer surfaces is highly undesirable because it is a poor conductor of heat. Scale formation results in reduced efficiency, and causes circulation restrictions in boilers and other water systems. Even very thin scale deposits may cause equipment failure under the severe operating conditions existing in this technical era. Uneven scale deposits may lead to pitting corrosion of the metal surfaces.

In the case of boilers, scale offers resistance to the flow of heat from the metal to the water. This may cause overheating of some areas in the boiler. These hot spots can lead to the failure of

equipment and unscheduled outages. In the case of cooling water systems, the presence of scale reduces the rate of heat transfer from the equipment to the cooling water and may cause equipment burnout and failure.

The common methods employed to prevent or minimize the formation of scale are:

- (1) External treatment of the feed water, i.e., softening the feed water before it enters the boiler or cooling water system.

- (2) Internal treatment of the feed water inside the boiler or cooling water system. In this case, the feed water is pumped along with certain chemicals which react with the scale forming minerals inside the system. The result is the formation of soft, easily removable deposits instead of scale.

Even though chemical methods for treatment of feed water have been used for over half a century, these methods still have certain disadvantages such as:

- (1) Feed water composition has to be evaluated at regular intervals to determine the amount of chemicals needed for treatment.

- (2) The use of chemicals increases the risk of environmental pollution.

- (3) The use of the zeolite process for treatment results in feed water containing sodium bicarbonate. This increases the susceptibility of boilers to embrittlement with catastrophic results.

- (4) Feed water treatment has to be changed depending upon

the design, heat transfer rate, and operating pressure of the equipment.

(5) In once-through cooling water systems, softening feed water is not economically feasible.

Recent research at Aqua Dynamics Corporation has resulted in the development of a new device which is believed to control and prevent the formation of scale. This device is called the quantum electrodynamic device (QED) since it injects small amounts of electromagnetic energy into the heat transfer system. The QED emits radio frequency (RF) waves in the range of 42.7 to 43.5 MHz, at a given amplitude into the heat transfer system. The minute amounts of energy injected into the water is believed to change the bonding characteristics of the scale forming ions, thus leading to the control and prevention of scale.

The use of QED for the prevention of scale formation offers the following advantages over conventional methods:

- (1) Reduction in expenses for water treatment.
- (2) Handling of chemicals and risk of environmental pollution is greatly reduced.
- (3) There is no need for determining feed water composition at regular intervals.
- (4) Risk of embrittlement of boiler surfaces is greatly reduced.
- (5) Savings in operating expenses because of the reduction in the number of blowdown procedures.

However, there is no significant data or evidence regarding the

application of RF waves for the treatment of water to prevent scaling. This has limited the applicability of the QED to a certain extent. This work is one of the first major attempts to study the effect of RF treatment of water on scale formation in a heat transfer system.

The major purpose of this research was to investigate the ability of the QED to control and prevent the formation of scale. Carbon steel specimens were exposed to supersaturated calcium carbonate solution for extended periods. In the control experiments, the QED was not activated. In the test experiments, the QED was activated. Immersion corrosion tests, particularly mass loss tests were used to evaluate general corrosion rates of the specimens. Electrochemical impedance spectroscopy (EIS) was used periodically to obtain information on the formation of scale layers and the corrosion rates. Microscopy was used to study the surface conditions of the specimens after exposures.

CHAPTER II

LITERATURE REVIEW

2.1 Mechanism of Scale Formation

Scale can be deposited in water systems in various ways. In general, when water flowing through a heat transfer system becomes supersaturated with respect to scale forming minerals or salts, these precipitate as scale. Deposition and growth of scale layers is mainly due to the decrease in the solubility of scale forming salts with increase in temperature. Figure 2.1 shows a section of an iron pipe with scale formed due to circulation of water through it.

The film of water immediately in contact with the heat transfer surface is at a higher temperature than the central portion of water. Since the solubility of scale forming salts decreases with increasing temperature, scale is first formed on the metallic surface. In the case of cooling water systems, feed water which is nearly saturated with one or more of the scale forming salts at room temperature, may come in contact with a hot surface. This may make the water supersaturated with respect to some salts and scale will form on the metal surface.

In the case of boilers, feed water is continuously added as steam is produced. This results in an increase in the concentration of scale forming salts as time passes. The increase can only be limited by using blowdown procedures at regular intervals. Blowdown is the

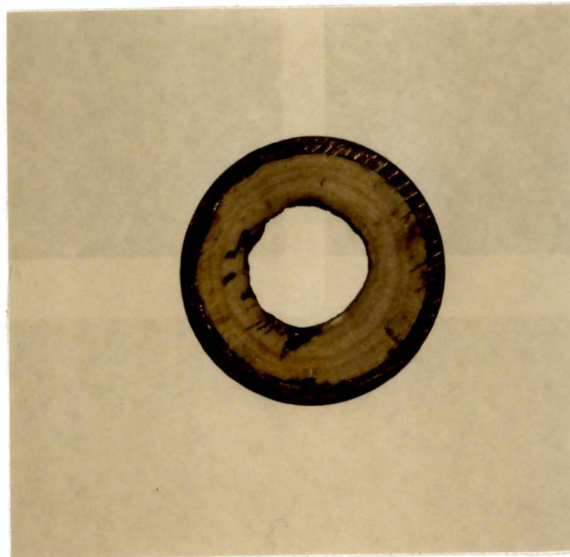


Figure 2.1 Section of an iron pipe with scale formed due to water circulation.

removal of water from a boiler system. Even though blowdown procedures are employed, the boiler water sometimes becomes supersaturated with scale forming salts under the existing conditions of pressure and temperature. As a result, precipitation takes place in the form of scale deposits.

According to Patridge[1], scale in boiler tubes can be deposited in more than one way. Settling of suspended or precipitated scale particles can occur on the surface, or some scale particles may be trapped in the surface irregularities. These settled particles conglomerate into a dense adherent scale with the passage of time. In other cases, scale can be deposited on the boiler surface by spontaneous crystallization of scale forming salts from supersaturated water. This spontaneous crystallization relieves the water film adjacent to the boiler surface from supersaturation temporarily. In a third case, scale is formed due to the evaporation of water to form bubbles. When bubbles are formed, the excess salts are deposited on the surface as scale.

In the case of water systems made up of iron or steel, it is believed that the scale formation is a result of two processes[2]. One process is the corrosion of the metal substrate while the other process is the deposition of calcium carbonate or other scale forming salts. In the initial stages, corrosion of the metal surface takes place leading to the formation of ferrous hydroxide which is subsequently oxidized to ferric oxide. If the carbonate content of the water is high, then ferrous carbonate also may be formed. This iron compound

layer provides nuclei for the crystallization of scale forming salts. The scale layer then grows on the iron compound layer at a rate which is influenced, among other factors, by the degree of supersaturation of water with respect to scale forming salts.

Once there is an initial deposit of scale crystals, growth of the scale layer can take place in more than one way[1]. The existing scale crystals which are in continuous contact with supersaturated water may continue to grow into large crystals in a direction perpendicular to the metal surface. If the initial deposit of scale crystals is covered by a layer of biofilm or some other layer which has been adsorbed onto it, then it loses direct contact with the supersaturated solution. In this case, deposition of small scale crystals takes place on the adsorbed layer due to crystallization or due to formation of bubbles. Scale crystals formed in this way will have a random orientation.

The rate of scale formation is related to the rate of decrease in the solubility of scale forming salts with increase in temperature. Another factor influencing the rate of scale formation is the rate of heat transfer across the surface on which the scale is growing. The rate and the type of flow (laminar or turbulent) of water in the system may also exert an influence on the rate of scale formation[3]. The degree of supersaturation of feed water also influences the rate of scale formation. The rate of scale formation is also influenced by the amount of scale forming salts present in the feed water. The growth of scale is accelerated by the effect of friction on the waterside of any system, since velocities along the surface are lower

than those near the central portion[4].

2.2 Factors Affecting Scale Formation

The formation of scale in water systems is affected by a number of factors such as:

(1) Temperature: Increasing temperature in many cases leads to an increase in the scale forming tendency of a water. This is the result of the decreasing solubility of many scale forming salts with increase in temperature. Figure 2.2 shows the influence of temperature on the solubility of calcium carbonate.

(2) Alkalinity and pH: These exert a great influence on the scale forming tendency of a water. As alkalinity is increased calcium carbonate becomes less soluble. Thus high alkalinity values result in the precipitation of calcium carbonate.

(3) Carbon dioxide partial pressure: The amount of carbon dioxide in the water is an important factor. Figure 2.3 shows that the solubility of calcium carbonate increases with increase in carbon dioxide partial pressure.

(4) Oxygen concentration: The amount of oxygen has an indirect effect on the precipitation of calcium carbonate[5]. An increase in the oxygen concentration causes a relative decrease in the carbon dioxide concentration leading to the precipitation of calcium carbonate.

(5) Feed water composition: Feed water composition can vary from source to source. The presence of uncommon ions in the feed water increases the solubility of scale forming salts such as calcium

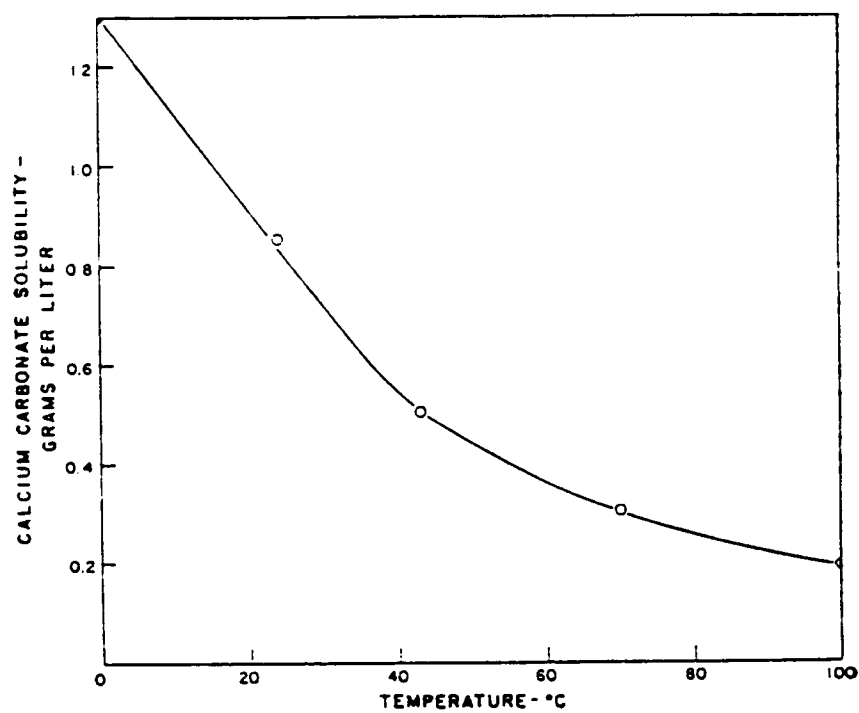


Figure 2.2 Effect of temperature on the solubility of calcium carbonate at 0.987 atm carbon dioxide pressure[6].

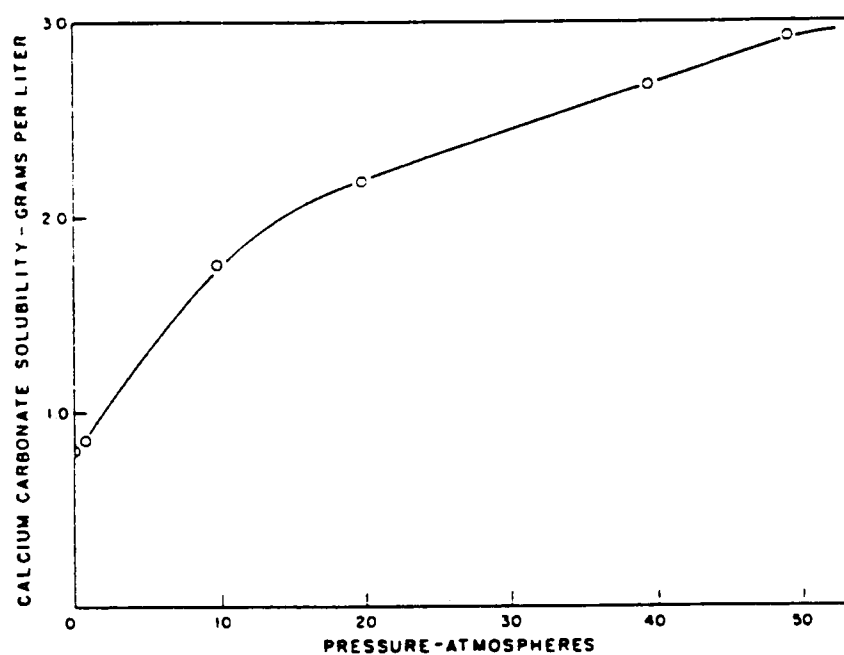


Figure 2.3 Effect of carbon dioxide partial pressure on the solubility of calcium carbonate in water[6].

carbonate and calcium sulphate[6]. The greater the amount of dissolved scale forming salts in the water, the higher is the scale forming tendency of water.

(6) Chemical additives: Chemicals such as phosphates are sometimes added as corrosion inhibitors. If the concentration of these phosphates is high the phosphate ions might combine with iron or calcium ions to form insoluble compounds which may be deposited as scale[7].

2.3 Constituents of Scale

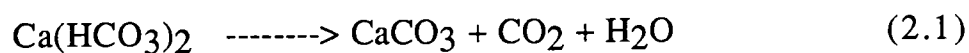
Scale resulting from natural water predominantly consists of carbonates and sulphates of calcium and magnesium, and to a lesser extent silicates. Of these, calcium carbonate is the primary constituent making up about 80% of most scales. Calcium sulphate, magnesium salts, and silicates constitute a majority of the remaining 20%. Salts of other metals also contribute to the deposits under certain conditions. Sometimes corrosion products of the metal also contribute to scale formation.

Calcium carbonate: The primary constituent of many scales formed from natural water is calcium carbonate. It exists in two crystalline forms, namely calcite and aragonite. Of these two, calcite is the more stable form at 77 F or ambient temperature[8].

The solubility of calcium carbonate in water decreases with increase in temperature. Figure 2.2 shows the influence of temperature on the solubility of calcium carbonate. The solubility of

calcium carbonate in distilled water at 25 C with a carbon dioxide partial pressure of $10^{-3.5}$ atm (open to atmosphere) is 0.050 g/liter. The solubility is also influenced by the carbon dioxide partial pressure, and the concentrations of other salts. The effect of carbon dioxide partial pressure on calcium carbonate solubility is shown in Figure 2.3.

Calcium carbonate exists in water as calcium ions and bicarbonate ions rather than as calcium ions and carbonate ions. The chemical reaction involved in the formation of calcium carbonate from calcium bicarbonate is given below:

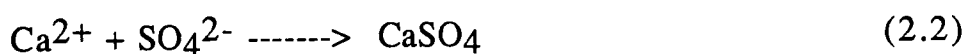


When water containing calcium bicarbonate is heated, carbon dioxide present is expelled. The solubility of calcium bicarbonate decreases with decrease in carbon dioxide content. As a result calcium bicarbonate decomposes to form a precipitate of calcium carbonate in the form of scale. This can be seen by applying the LeChatelier principle to Equation 2.1. As the carbon dioxide concentration decreases, the reaction is shifted to the right in Equation 2.1. Thus, calcium bicarbonate decomposes to restore the equilibrium. If the carbon dioxide concentration is decreased in another manner, such as by increasing the oxygen content, then again the precipitation of calcium carbonate occurs leading to scale formation.

The presence of salts with uncommon ions in the water generally tends to increase the solubility of calcium carbonate[6].

This is the result of the increase in ionic strength of water, which affects the solubility product of calcium carbonate.

Calcium sulphate: Calcium sulphate forms a hard, dense, highly adherent scale which is very difficult to remove. The effect of temperature on the solubility of calcium sulphate is shown in Figure 2.4. Calcium sulphate is precipitated directly due to its insolubility at high temperature. The precipitation of calcium sulphate takes place as:



The presence of other salts also has an influence on the solubility of calcium sulphate. The solubility of calcium sulphate in distilled water is about 2.1 g/liter at 25 C.

Magnesium salts: Magnesium salts such as magnesium carbonate and magnesium hydroxide constitute a notable percentage of some scales. Magnesium carbonate is precipitated due to the decomposition of magnesium bicarbonate. The solubility of magnesium carbonate decreases with increase in temperature, and increases with increase in carbon dioxide content. The solubility of magnesium carbonate is about 0.22 g/liter. Thus, the chances that calcium carbonate precipitates before magnesium carbonate are greater because of the higher solubility of magnesium carbonate in water. At very high temperatures near the boiling point of water magnesium carbonate decomposes to form magnesium hydroxide, and magnesium hydroxide scale is deposited. The solubility of magnesium hydroxide decreases with increase in temperature. The

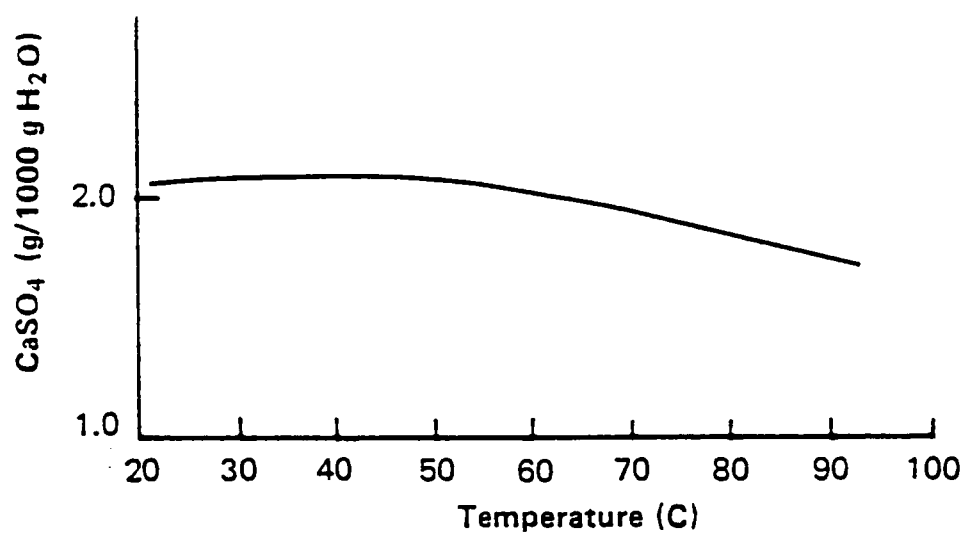
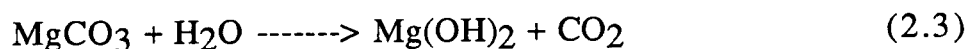


Figure 2.4 Effect of temperature on the solubility of calcium sulphate in water[6].

decomposition of magnesium carbonate to magnesium hydroxide takes place in the presence of water as given below:



Iron compounds: Deposition of iron compounds such as ferric oxide and ferrous carbonate as scale is due to the high iron content of feed water and due to the corrosion of iron and steel components. The corrosion product of iron is deposited as ferric oxide which adheres to the metal surface along with other scale forming salts. Iron compounds such as ferrous carbonate are also found in some scales formed from water with very high carbonate content. Bacteria such as gallionella ferruginea cause soluble iron to be deposited as ferric hydroxide which is subsequently oxidized to ferric oxide[7].

Silicates: Most of the silicate scales are formed at temperatures above the boiling point of water, when evaporation takes place. Even though silica occurs in small quantities in scale, it acts as an excellent binding agent in the formation of scale.

2.4 Scale Predicting Indices

The scale forming tendency of a water with respect to calcium carbonate can be predicted using one of the many indices available.

Langlier[9] in 1936 proposed an index called the Langlier Index or the Saturation Index (SI). The SI is given by the following equation.

$$\text{SI} = \text{pH} - \text{pH}_s \quad (2.4)$$

$$\text{pH}_s = \text{pK}'_2 - \text{pK}'_s + \text{pCa}^{2+} + \text{pAlk} \quad (2.5)$$

In the above equations, pH stands for the actual pH of the water, pH_s stands for the pH at which a water of given calcium content and alkalinity is in equilibrium. In general pX denotes the negative logarithm of "X". K'_s is the solubility product of calcium carbonate, K'_2 is the ionization constant for the reaction



Ca^{2+} stands for the calcium concentration in moles/liter. Alk is the total alkalinity expressed as equivalents per liter of titrable base to the methyl orange end point.

If the SI is negative, it means that the water is undersaturated with respect to calcium carbonate. If SI is zero then the water is in equilibrium with respect to calcium carbonate. If SI is positive then the water is supersaturated with respect to calcium carbonate.

Larsen and Buswell[10] later on came up with a modification of the equation proposed by Langlier to include compensation for variations in temperature and salt concentration. The index (I) is given by the following equation:

$$I = \{pH + \log(Ca^{2+}) + \log(Alky) - (pK'_2 - pK'_s) - 9.30 - ((2.5 \sqrt{u}) / (1 + 5.3 \sqrt{u} + 5.5u))\} \quad (2.7)$$

where u denotes the ionic strength, Ca^{2+} is the concentration of calcium ions expressed in ppm as calcium carbonate, and Alky is the alkalinity expressed in ppm as calcium carbonate.

Ryznar[11] came up with another index called the stability index which indicates not only the scaling tendency of water, but also

gives a semiquantitative value for the amount of scale that may be deposited. The stability index is given by:

$$\text{Stability Index} = 2\text{pH}_s - \text{pH} \quad (2.8)$$

$$\text{pH}_s = \{(\text{pK}'_2 - \text{pK}'_s) - \log(\text{Ca}^{2+}) - \log(\text{Alky}) + 9.30 \\ + ((2.5 \sqrt{u}) / (1 + 5.3 \sqrt{u} + 5.5u))\} \quad (2.9)$$

A stability index of six means that the water is in equilibrium. A stability index of less than six means that the water is supersaturated with respect to calcium carbonate. A stability index greater than six means that the water is undersaturated with respect to calcium carbonate.

2.5 Fundamentals of Corrosion

Corrosion may be defined as the deterioration of materials which occurs because of the interaction between the material and its environment. Corrosion is electrochemical in nature. The electrochemical nature of corrosion can be illustrated by considering the case of iron in aerated acidic and basic solutions.

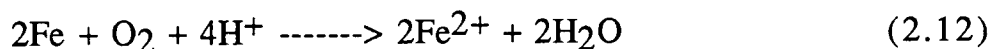
In aerated acidic solution the anodic reaction is the oxidation of iron as given below.



The overall cathodic reaction is



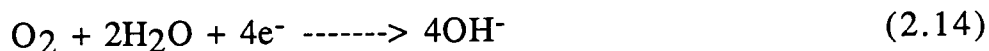
The overall reaction is



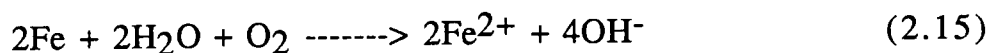
In the case of iron in aerated neutral or basic solutions the anodic reaction is



The overall cathodic reaction is



The overall reaction is



2.6 Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) is a relatively new technique that can be used to obtain kinetic and mechanistic information in a corrosion process. Since the formation of scale is believed to inhibit the corrosion process, EIS was employed in this study. EIS uses very small excitation signals in the range of 5-10 mv peak-to-peak and will not disturb the working electrode surface.

Theory: The basic principle behind EIS is that electrochemical interfaces can be viewed as combinations of passive circuit elements such as resistors, capacitors, and inductors. Thus, a purely electronic model can be used to represent the electrochemical cell[12].

A convenient way to express the impedance of any circuit element in a complex form is to use the complex number, $j = \sqrt{-1}$. Thus, for a pure resistor:

$$Z = R + 0j \quad (2.16)$$

For a pure capacitor:

$$Z = 0 - j/\omega c \quad (2.17)$$

For a pure inductor:

$$Z = 0 + j\omega L \quad (2.18)$$

In the above equations, Z represents the impedance, ω is the angular frequency, R is the resistance, C is the capacitance, and L is the inductance. Figure 2.5 shows the representation of the real and imaginary parts of Z in the form of an Argand diagram.

The absolute magnitude of impedance is given by the expression:

$$Z = \sqrt{(Z')^2 + (Z'')^2} \quad (2.19)$$

In the above equation

$$Z' = |Z| \cos\theta$$

$$Z'' = |Z| \sin\theta$$

where θ is the phase angle.

In the complex form,

$$Z = Z' + jZ'' \quad (2.20)$$

Equivalent circuit: The concept of an equivalent circuit provides the relation between the observed impedance and the electrochemical process going on at the interface. The equivalent circuit is an electronic model consisting of electrical circuit elements that behave in a manner similar to a reacting interface.

A simple equivalent circuit proposed by Randles[13] for a simple corroding surface is shown in Figure 2.6. In this circuit, R_s is the uncompensated resistance between the working electrode and the reference electrode, R_p is the polarization resistance or charge

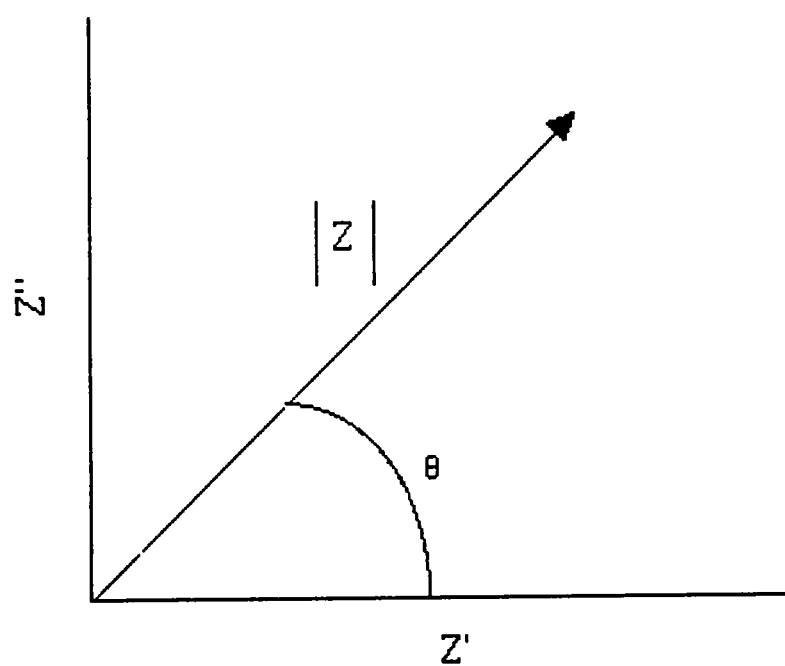


Figure 2.5 Argand diagram showing the real and imaginary parts of impedance.

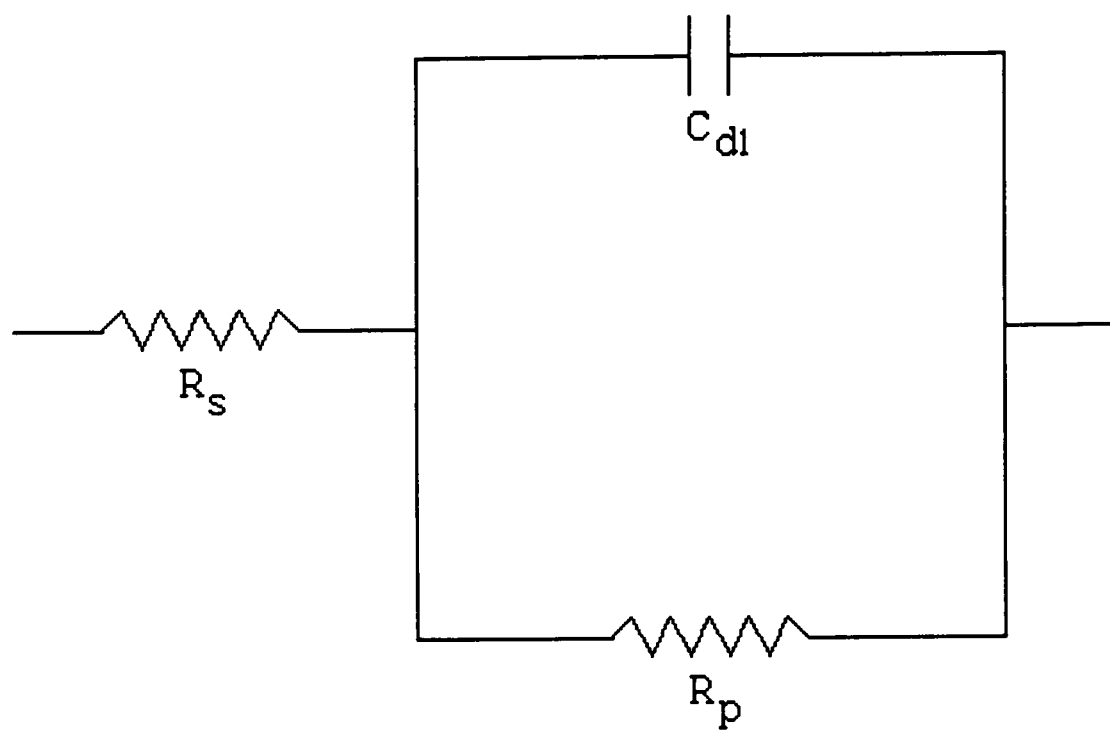


Figure 2.6 Equivalent circuit for a simple corroding surface.

transfer resistance, and can be used as a measure of the charge transfer rate. C_{dl} is the double layer capacitance at the interface. Knowledge of R_p gives the corrosion rate. Knowledge of C_{dl} gives revealing information regarding the phenomena of adsorption, desorption, or film formation on the surface of the working electrode. The parallel combination of R_p and C_{dl} in Figure 2.6 represents the corroding interface.

EIS can be used to obtain the values of the various electrical elements in a proposed equivalent circuit for an electrochemical system. In other cases, it can be used to generate an electronic model from the data obtained. However, because of the nature of electrochemical systems, sometimes the same result can be obtained through different combinations of electrical circuits.

Data analysis: The impedance of any system will vary with angular frequency. One useful method to depict this frequency dependence of impedance is to use the Nyquist plot. Figure 2.7 shows a Nyquist plot for the simple circuit shown in Figure 2.6. The Nyquist plot consists of a set of points on the complex plane, each defined by the real part and the imaginary part of the corresponding impedance data obtained at a specific frequency. From the Nyquist plot shown in Figure 2.7, it is clear that at high frequencies the impedance is entirely due to the uncompensated resistance, while at low frequencies it approaches the sum of R_p and R_s . Between these two extremes, the frequency dependence of impedance is caused by the capacitive element C . However, one problem with Nyquist plots is

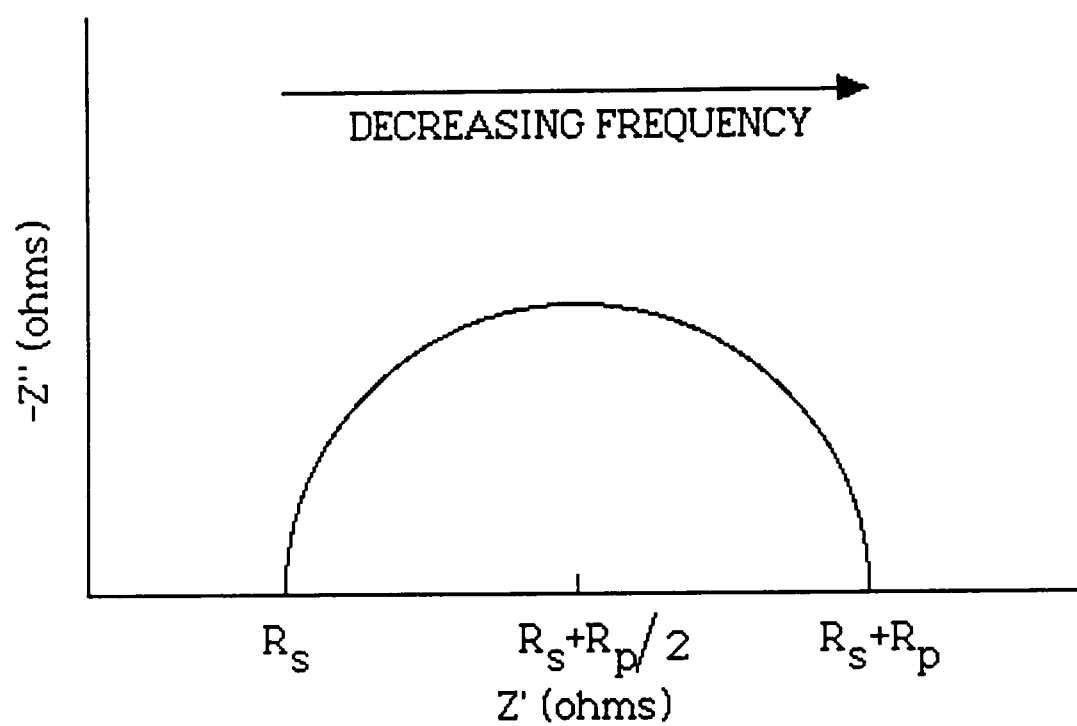


Figure 2.7 Nyquist plot for the equivalent circuit shown in Figure 2.6.

that frequency is not plotted explicitly. According to Mansfield[14], polarization resistance in EIS is given by the difference of the measured impedance at high frequencies and low frequencies. The rate of corrosion can then be calculated using the Stearn-Geary[15] equation given below:

$$i_{\text{corr}} = \frac{\beta_a \beta_c}{2.303 A (\beta_a + \beta_c) R_p} \quad (2.21)$$

In the above equation, β_c and β_a are the cathodic and anodic Tafel slopes respectively, A is the exposed area of the working electrode, and R_p is the polarization resistance.

The current density obtained from Equation 2.21 can be used to obtain the corrosion rate, based on Faraday's law[16], as given below:

$$\text{Corrosion rate (mpy)} = \frac{0.13 \times i_{\text{corr}} (\text{uA/cm}^2) \times \text{E.W.}}{\text{density (g/cm}^3\text{)}} \quad (2.22)$$

where E.W. is the equivalent weight in grams.

The Bode plot shown in Figure 2.8 is another method to plot and analyze impedance data. In this, the variation of impedance and phase angle with frequency are presented. Thus, the Bode plot shows how the impedance varies with frequency. The Bode plot can also be used to obtain values of polarization resistance and uncompensated resistance. Bode plots are more useful when there is more than one rate determining step in the electrochemical process. The different steps can be detected easily from the Bode plots. It is easier to

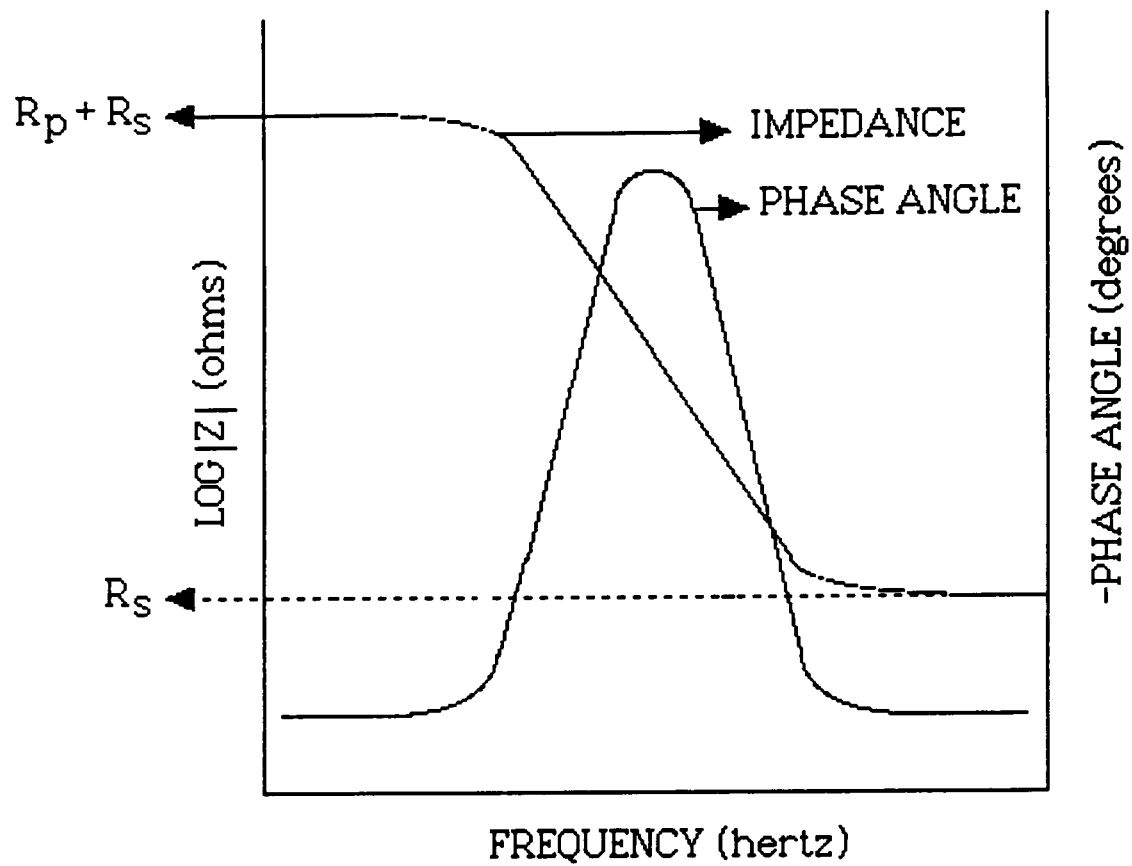


Figure 2.8 Bode plot for the equivalent circuit shown in Figure 2.6.

observe multiple time constants in Bode plots than in Nyquist plots.

Measuring techniques: EIS data is obtained by studying the response of the system over a range of frequencies. In the earlier days, most of the EIS measurements were made using the frequency domain methods, i.e., data was taken at each frequency point. But this method consumes a lot of time in data acquisition. Later on, the time domain technique was developed where the real and imaginary components were easily resolved. The fast fourier transform (FFT) techniques used now make use of an algorithm to apply simultaneously a complex mixture of excitation waveforms of various frequencies to the electrochemical system. The complex response obtained is then resolved to obtain data at discrete frequency points. A major advantage of the FFT technique is that data at low frequencies can be obtained at a faster rate than with other methods.

CHAPTER III

EXPERIMENTAL PROCEDURES

3.1 Material

The material used for all experiments was very high-quality low carbon steel. Figure 3.1 shows the microstructure of the low carbon steel used for all experiments. The 0.6 mm thick parent material was cut into 2 cm x 2 cm test specimens.

3.2 Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy was used to obtain kinetic information on the corrosion process and mechanistic information regarding the formation of scale. Sample preparation is extremely important for EIS because data obtained is very much influenced by the initial surface condition of the specimen.

The specimen preparation for EIS was done as described below. The carbon steel specimen was soldered to a brass screw as shown in Figure 3.2. This was done in order for the specimen to have electrical contact with the external instruments. The soldered specimen was then rinsed in acetone. The specimen was then mounted in Maraglass 655 epoxy (ACME Chemical and Insulation Co.), and cured at 80 C for 24 hours. After curing, the specimen was first ground on 120 grit silicon carbide paper and was finished by polishing on 600 grit silicon carbide paper. In order to avoid crevice corrosion at the interface of the epoxy and the specimen, the interface was coated

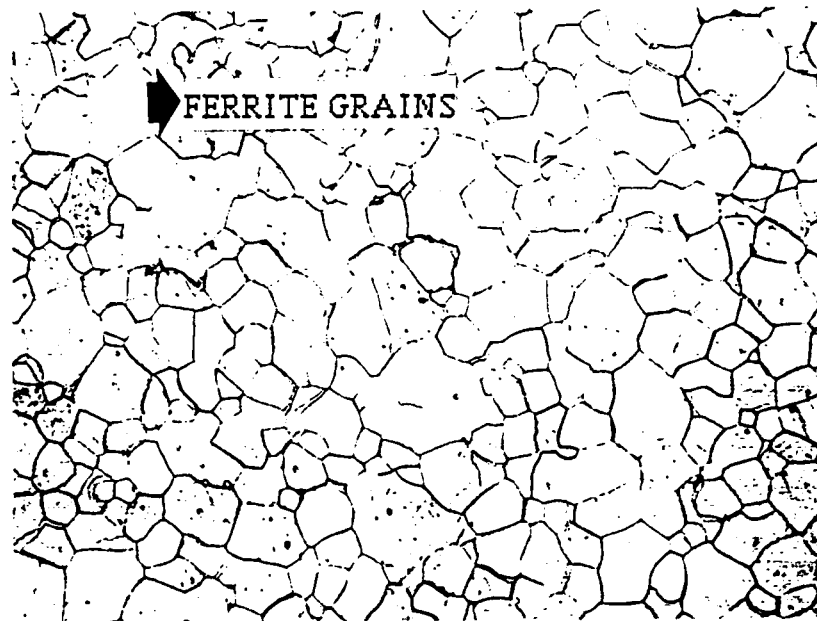


Figure 3.1 Photomicrograph showing the microstructure of the low carbon steel used for experiments (Magnification: 400X).

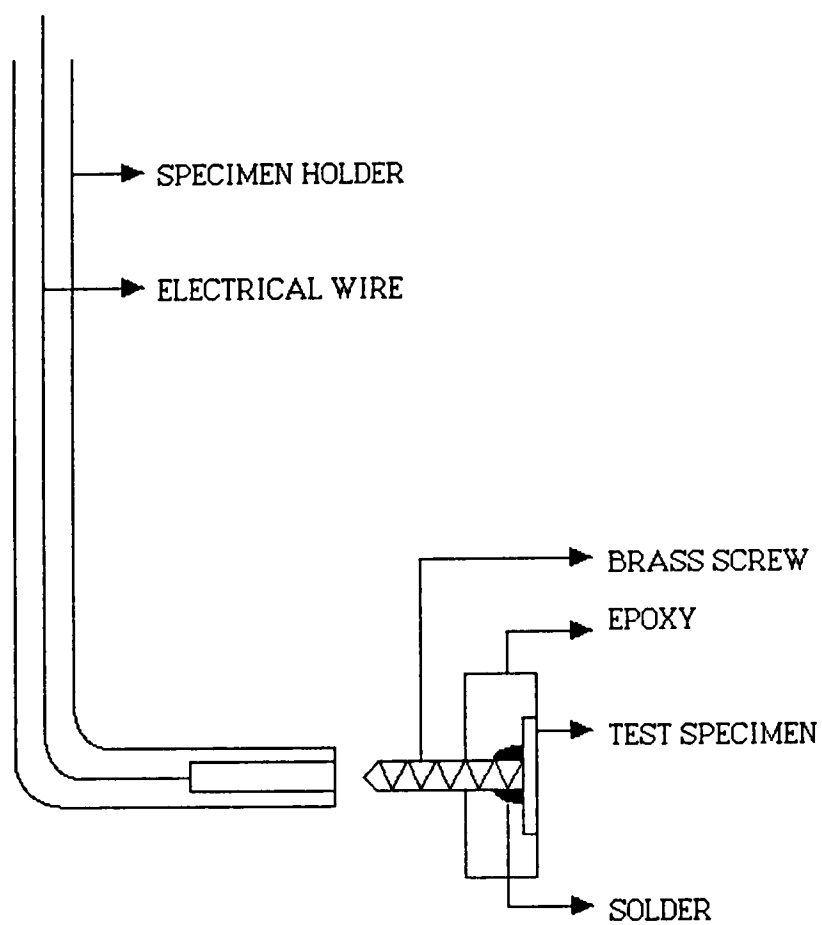


Figure 3.2 Schematic representation of the working electrode with specimen.

with Amercoat 90 (Ameron Co.) leaving an exposed area of about 3 cm^2 on the surface of the specimen. The specimen was again cured in an oven at 80 C for 4 hours so as to dry the Amercoat 90 coating. The exposed surface of the specimen was then polished with a polishing cloth using 9 micron diamond paste to remove any oxide film formed before the specimen was introduced into the electrochemical cell.

The set up used for the EIS measurements is shown in Figure 3.3. The primary cell employed was a typical electrochemical cell with an assembly of working, reference, and counter electrodes. The test medium employed was a supersaturated solution of calcium carbonate. The pH of the test medium employed was in the range of 8.4 to 8.6. Tap water from the University of Tennessee, Knoxville water supply system was used to prepare the test medium.

The primary cell was made air tight and was connected to a secondary cell through a tygon tube. The secondary cell was equipped with a sparger for continuously sparging the test medium with air. The secondary cell was also equipped with an air outlet. The secondary cell was connected to a reservoir holding the test medium, through a tygon tube. A centrifugal pump was connected to the secondary cell to pump the test medium from the secondary cell to the primary cell. Both the primary and secondary cells were of 2 liter capacity. The leads from the QED were connected to two stainless-steel threaded-bolt electrodes which were inserted through the secondary cell top. The two electrodes (0.3 cm diameter) were placed

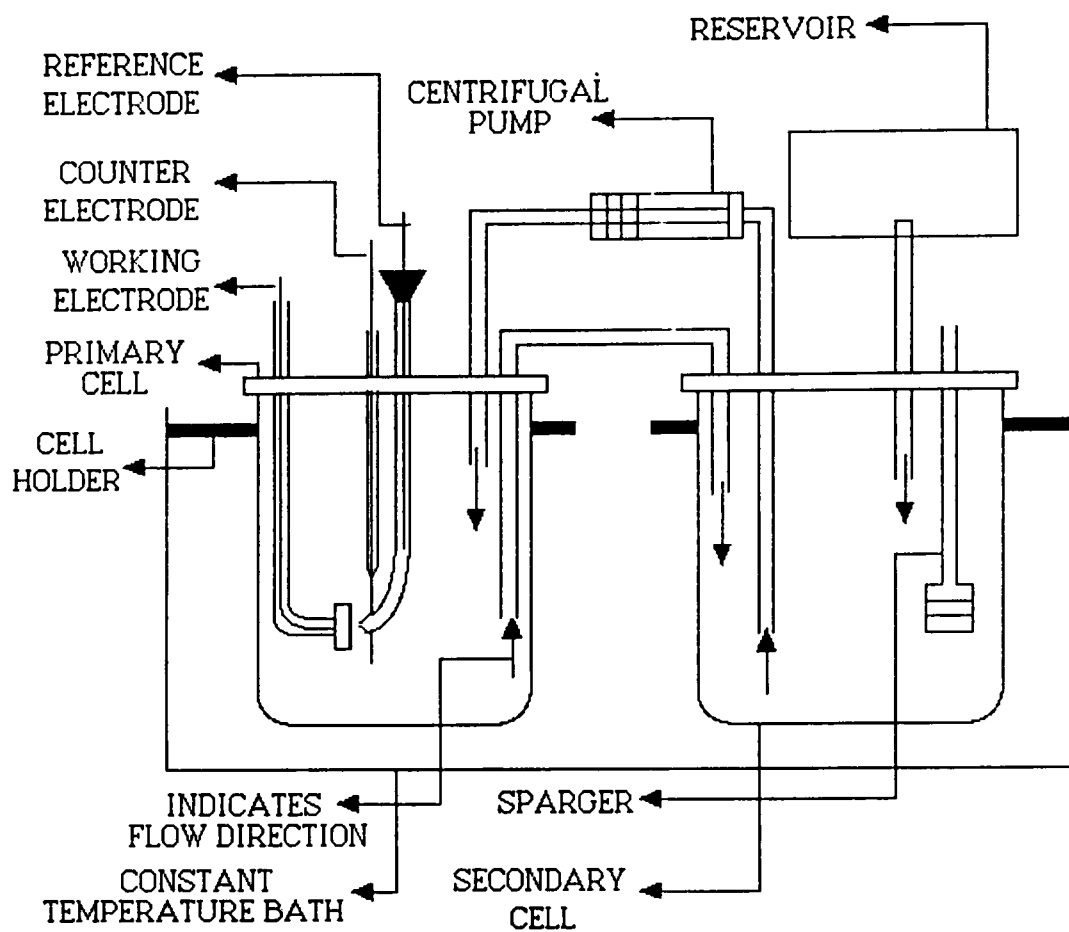


Figure 3.3 Schematic diagram of the experimental set up used for EIS and immersion tests.

8.2 cm apart, and were immersed in the test medium to a depth of 3 cm.

To start the experiment, the assembly of electrodes was introduced into the primary cell. The primary cell was then sealed completely, with a cell top to make it air tight. Then the inlet to the secondary cell from the reservoir was opened allowing the test medium to enter the secondary cell. Once the test medium reached a certain level in the secondary cell, the centrifugal pump was switched on to pump the test medium into the primary cell. As soon as the primary cell was full, the excess test medium reentered the secondary cell through the tygon tubing, under pressure. When both the primary and secondary cells were full the inlet to the secondary cell was closed.

Once the experiment was started the test medium in the cells was allowed to circulate for 24 hours. The entire set up was maintained at a temperature of 50 C (122 F), using a constant temperature bath to aid the precipitation of calcium carbonate as scale. Further, the medium was continuously sparged with air. At the end of every 24 hours, the circulation was stopped and 3 liters of the test medium was replaced with freshly prepared test medium. EIS data were taken every 24 hours. Each experiment was performed for a period of 19 days. The period of 19 days was selected after having found that a reasonable amount of scaling occurred under controlled conditions in 19 days. In the control experiments, the QED was not activated. In the test experiments, the QED was activated. The waves

emitted from the QED were monitored on a cathode ray oscilloscope. The QED was found to be emitting radio waves in the frequency range of 42.8 to 43.1 MHz, with a peak-to-peak voltage amplitude of 22 to 24 V.

A saturated silver/silver-chloride electrode was used to supply a constant potential against which the potential of the working electrode was measured. EIS data were taken using an EG&G 273 Potentiostat, and an EG&G 5208 Lock-in-Amplifier in conjunction with a personal computer. Data were taken over a range of frequencies from 0.005 Hz to 100 KHz. The Lock-in-Amplifier was used to generate frequencies in the range 5 Hz to 100 KHz. The personal computer was used to generate frequencies in the range 0.005 Hz to 11 Hz. The data was directly transferred and stored on a floppy disk. A schematic representation of the connections among the various instruments is shown in Figure 3.4.

3.3 Immersion Tests

Mass loss tests were conducted by immersing carbon steel specimens in the test medium. Specimens of 2 cm x 2 cm size were cut from the parent material. A hole of about 0.4 cm in diameter was drilled in one corner of each specimen. Each specimen was ground on 240 grit silicon carbide paper. The specimen was then polished on 600 grit silicon carbide paper. The specimen was then cleaned in 5% HCl solution containing 1% rodine (Ameron Products, Inc.). The specimen was cleaned in this solution and weighed until the weight difference between consecutive measurements was less than 0.2 mg.

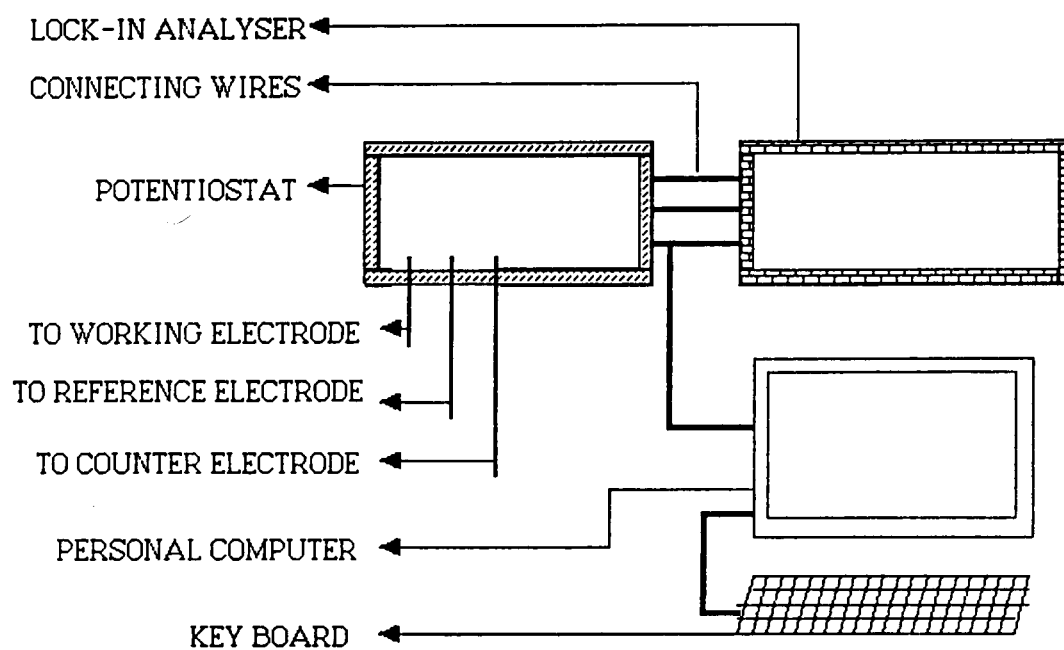


Figure 3.4 Schematic representation of the connections between the various instruments.

The experimental set up that was used for EIS measurements, was also used for the immersion tests. The specimens were suspended from a glass rod instead of being attached to the working electrode. After a given test period, each specimen was first cleaned in distilled water, and scrubbed to remove corrosion products and scale if any. The specimen was then cleaned in 5% HCl solution containing 1% rodine to remove the tightly adherent scale layers if any. Finally the specimen was again cleaned in distilled water, dried and then weighed.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Immersion Tests

The results from the mass loss tests are shown in Table 1. The mass loss per unit area obtained from the tests was converted to give the average corrosion rate in mils per year (mpy), using the conversion formula given below[17]:

Corrosion Rate (mpy) =

$$\frac{3.45 \times 10^6 \times \text{Weight Loss (gm)}}{\text{Area (cm}^2\text{)} \times \text{Density (gm/cm}^3\text{)} \times \text{Time (hrs)}} \quad (2.23)$$

The lowest corrosion rate of 6.40 mpy was shown by the specimen exposed to the test medium under control conditions (QED not activated). The corrosion rate for the specimen exposed to the test medium under test conditions (QED activated) was higher at about 10.35 mpy. The highest corrosion rate was shown by the specimen exposed to tap water (QED not activated).

The low corrosion rate exhibited by the specimen under control conditions was probably due to the formation of an adherent, porous scale layer. Visual observation of the specimen immediately after the test revealed the presence of two layers: a layer of corrosion product immediately adjacent to the metal surface, and a scale layer on top of the corrosion product. Similar observations have been made by other investigators[2]. It is believed that the porous scale layer on top of

Table 1. Immersion Test Results
19 Day Period, Temperature - 50°C

ELECTROLYTE	AVERAGE CORROSION RATE (mpy)
Saturated Calcium Carbonate Solution With QED Off	6.40
Saturated Calcium Carbonate Solution With QED On	10.35
Tap water With pH Adjusted to 8.5 - Specimen # 1	23.72
Tap Water With pH Adjusted to 8.5 - Specimen # 2	23.96

the corrosion product acted as a passive coating leading to a decrease in the corrosion rate. The corrosion rate obtained represents an average corrosion penetration rate (CPR) for the entire period of the test. The actual corrosion rate must have been higher during the initial period, and lower during the final period of the exposure. The corrosion reaction during the final period might have been taking place at the metal/electrolyte interface, and also at the metal/corrosion-product-scale-layer interface.

Similar observations as mentioned above were made for the specimen exposed to the test medium under test conditions, i.e., with the QED activated. However, this specimen exhibited a higher corrosion rate than the specimen under control conditions. This result was attributed to a more porous and a comparatively thin layer of scale formed on the specimen under test conditions. This observation tended to indicate that RF treatment of the test medium might in some way be slowing down the formation of scale.

The specimen exposed to tap water exhibited the highest corrosion rate. This was due to the fact that there was no additional layer of protection (scale) on top of the corrosion product.

Surface examination of the specimens after cleaning showed that the surfaces of all specimens were roughened due to corrosion. However the specimens differed in the degree of roughness. Figures 4.1 through 4.3 show photomicrographs of the test specimens taken after cleaning at 200X magnification. The specimen exposed to the test medium under control conditions showed the least degree of

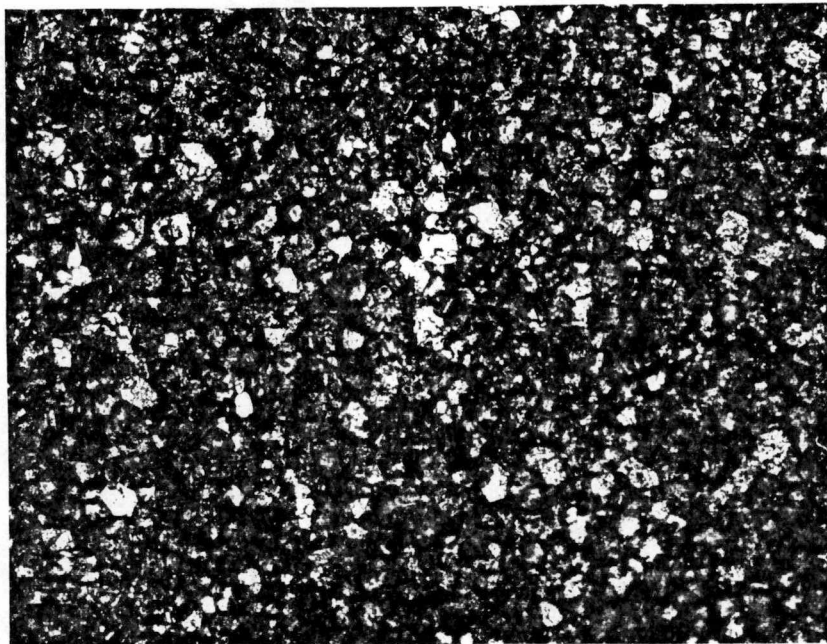


Figure 4.1 Photomicrograph of specimen immersed in test medium under control conditions after cleaning (Magnification: 200X).

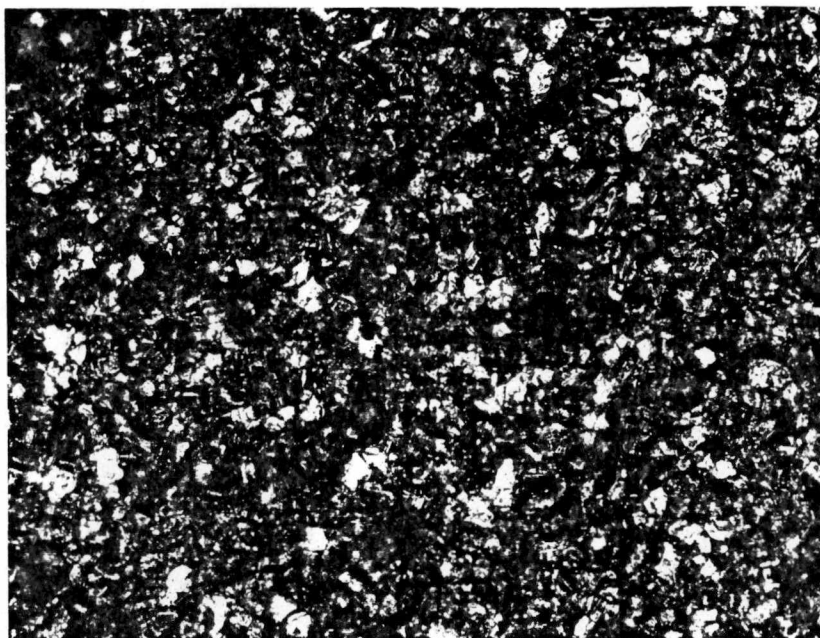


Figure 4.2 Photomicrograph of specimen immersed in test medium under test conditions after cleaning (Magnification: 200X).

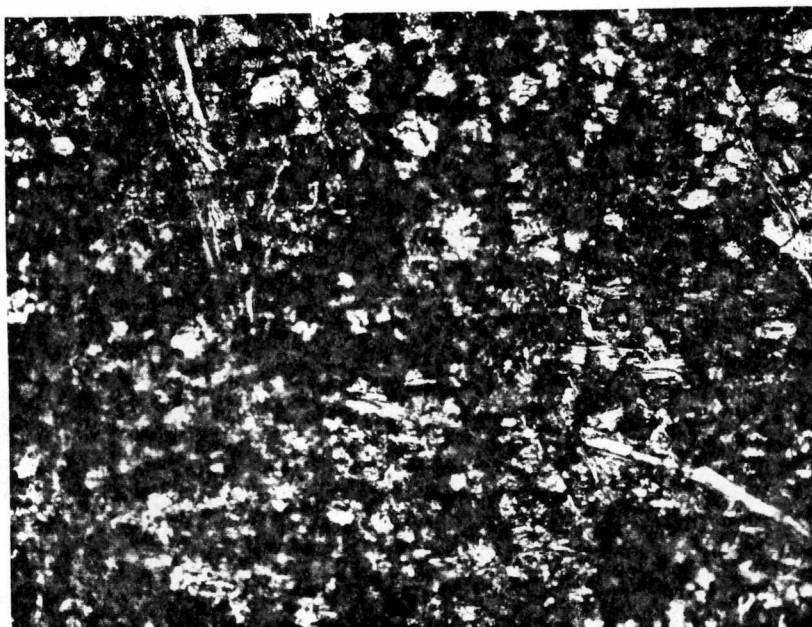


Figure 4.3 Photomicrograph of specimen immersed in tap water after cleaning (Magnification: 200X).

roughness. The specimen exposed to tap water showed the highest degree of roughness. The surface of this specimen was covered with abnormal elevations and depressions. This fact can be easily observed in Figure 4.3 in which some of the areas are out of focus due to abnormal elevations and depressions. The specimen exposed to the test medium under test conditions showed a degree of roughness in between the above two cases. All these observations supported the inferences drawn from the corrosion rates of the different specimens.

It is believed that the roughness on the surface of the specimens was caused due to the loss of metal because of the corrosion reactions. Hence the greater the corrosion rate the higher the degree of roughness. In the case of the specimen under control conditions, the active area available for the corrosion reaction must have become smaller with the passage of time, hence the low degree of roughness and corrosion rate. In the case of the specimen under test conditions, the active area available must have been comparatively larger. This difference in the extent of active areas was probably due to the difference in the nature of the scale layers formed on these two specimens. In the case of the specimen exposed to tap water, a very large active area must have been available when compared to the other two cases. This large active area was due to the absence of any adherent scale film. It is believed that the corrosion product formed was very porous and did not adhere well to the surface of the specimen. Hence, the corrosion rate and the degree of roughness were highest in this case.

4.2 Electrochemical Impedance Spectroscopy

The frequency responses of the specimens were studied under various conditions: in the test medium under control conditions, in the test medium under test conditions, in tap water, and in tap water with inhibitors. Complex plane plots for the specimens in the first two cases described above are shown in Figures 4.4 through 4.21. These impedance spectra were obtained at the end of each day for a period of 19 days. In both cases, the impedance spectra showed either partially resolved or completely resolved semicircles.

In the case of the specimen exposed to the test medium under control conditions, a single semicircle was seen in the complex plane plots obtained during the first two days. These semicircles were very much depressed, with their centers located well below the Z' axis. These depressed semicircles were probably due to the existence of more than one relaxation phenomenon at the interface[18]. However, in this case, the various relaxation phenomena could not be resolved. The negative values of the impedance at high frequencies were because of phase shifts arising from the potentiostat[19, 20]. This phase shift was due to the difference between the measuring resistor in the potentiostat and the impedance of the system being studied. Apart from this, the negative values of impedance did not indicate anything. With passage of time from the first day to the fourth day, it can be seen from the plots that the depression in the semicircles had become less pronounced. Further, the complex plane plot obtained on the third day showed a remarkable additional feature.

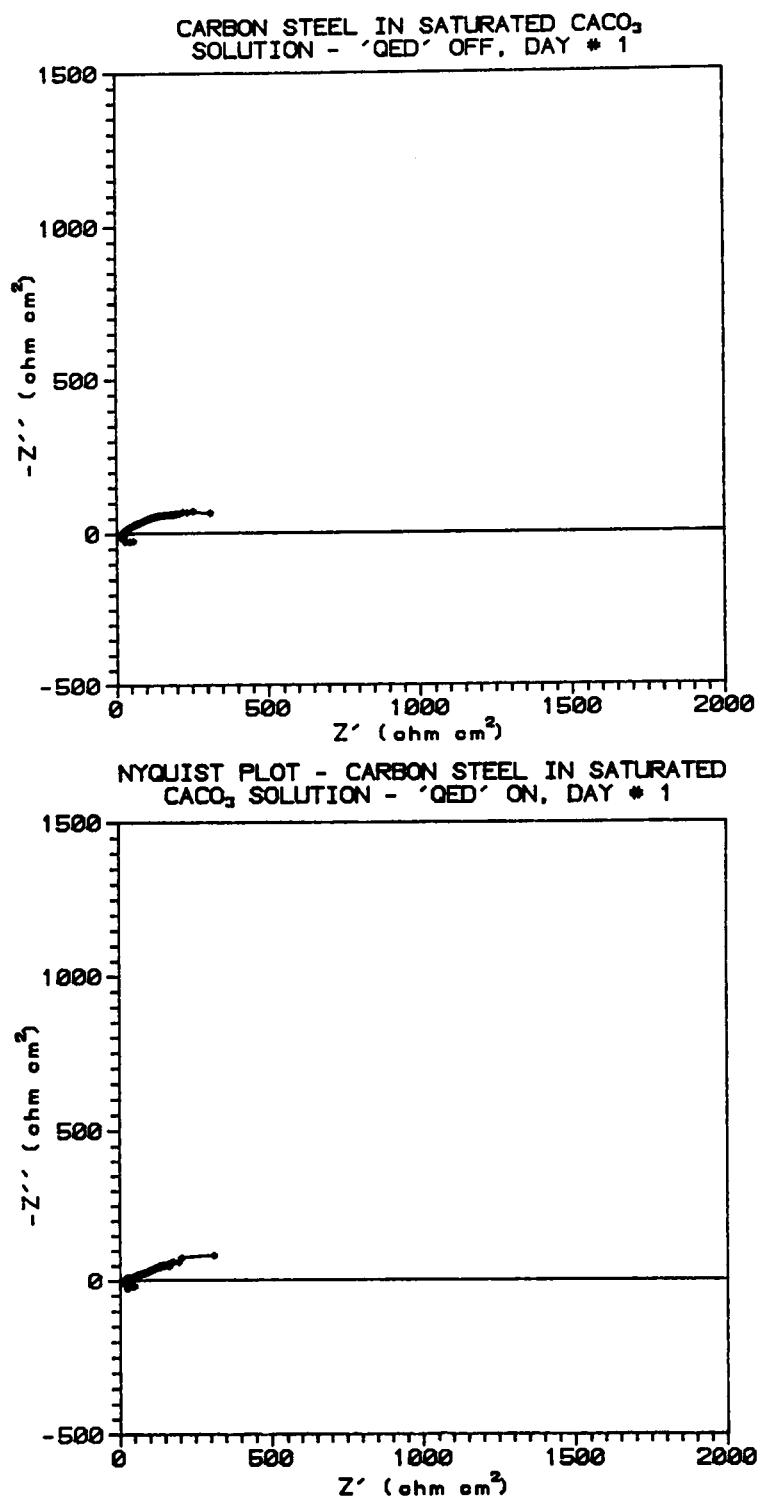


Figure 4.4 Complex plane plots for specimens under control and test conditions after day 1.

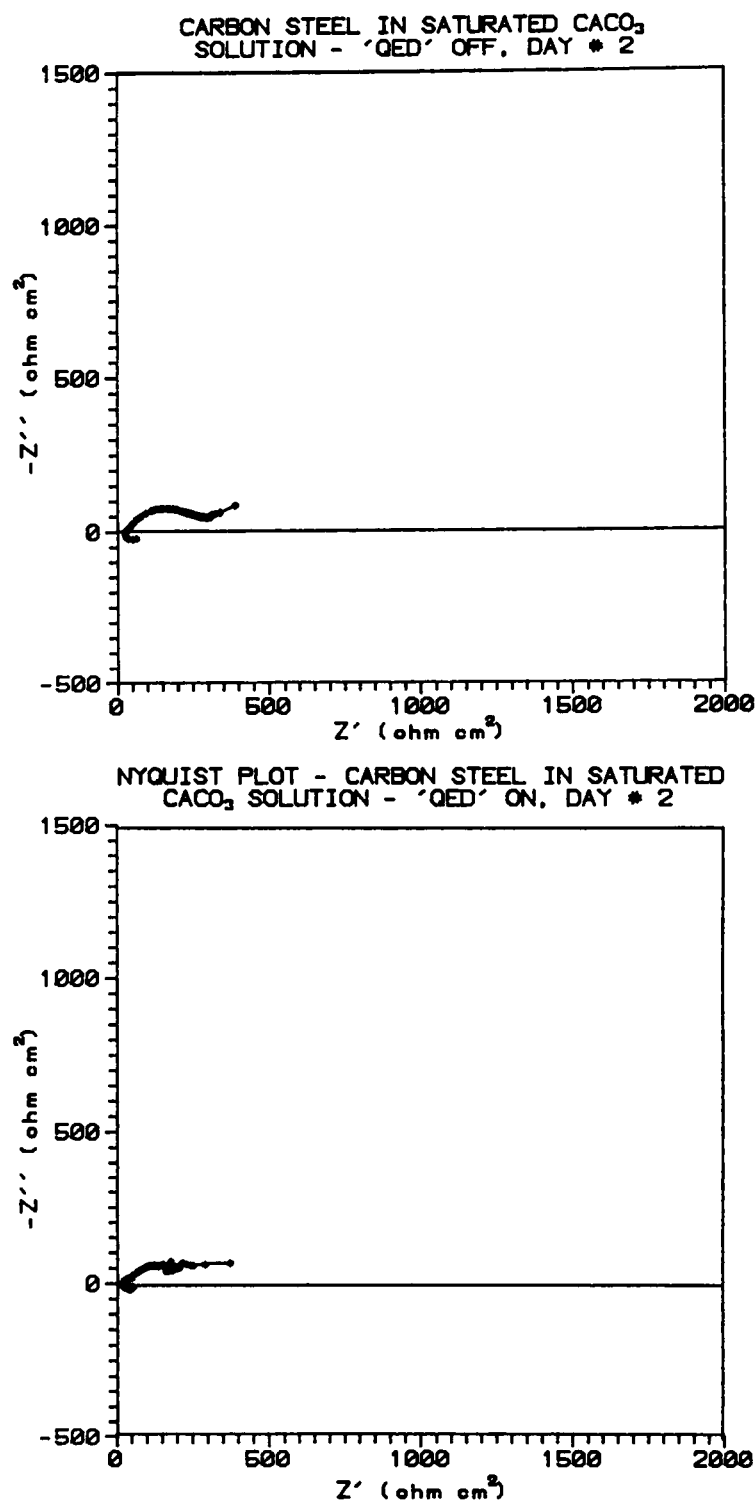


Figure 4.5 Complex plane plots for specimens under control and test conditions after day 2.

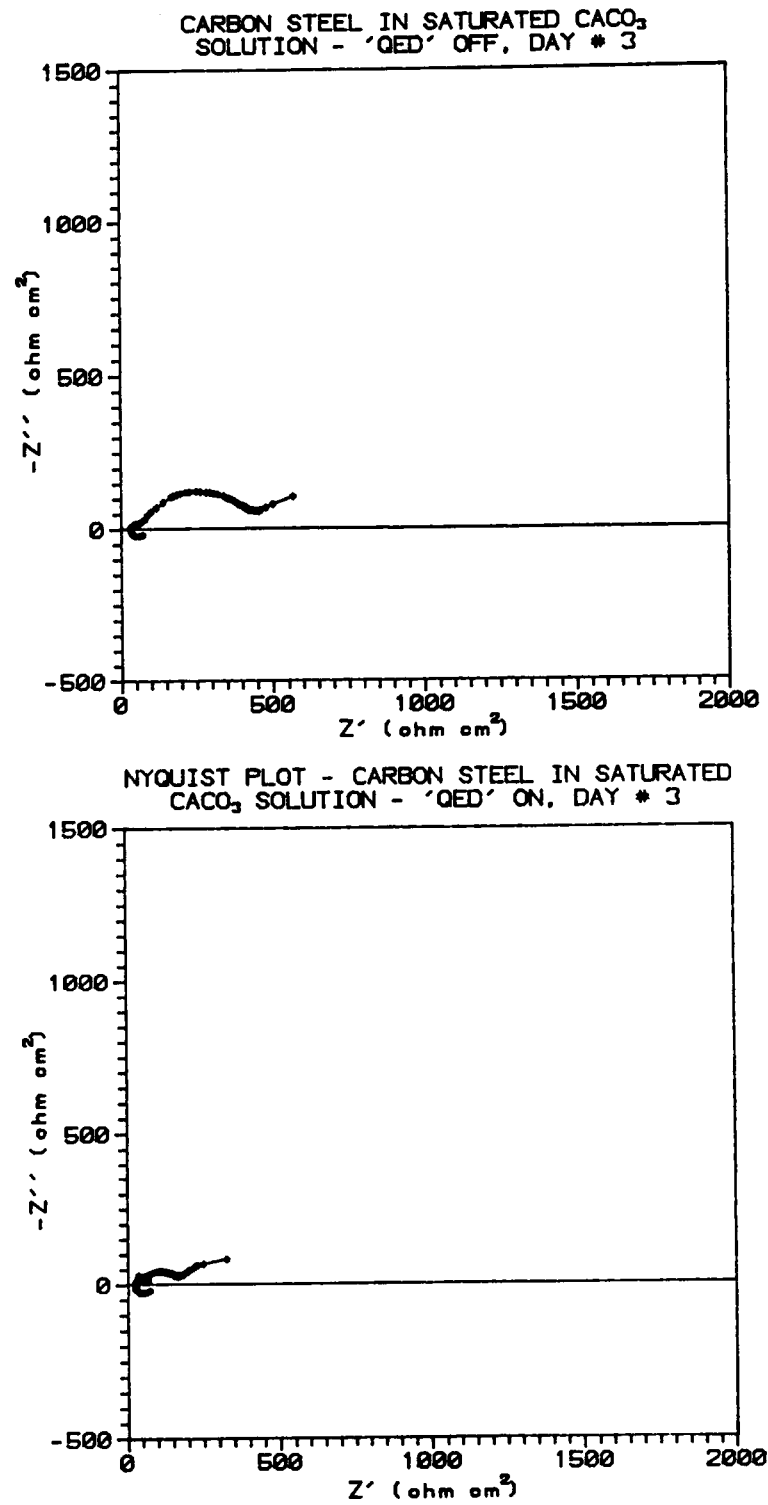


Figure 4.6 Complex plane plots for specimens under control and test conditions after day 3.

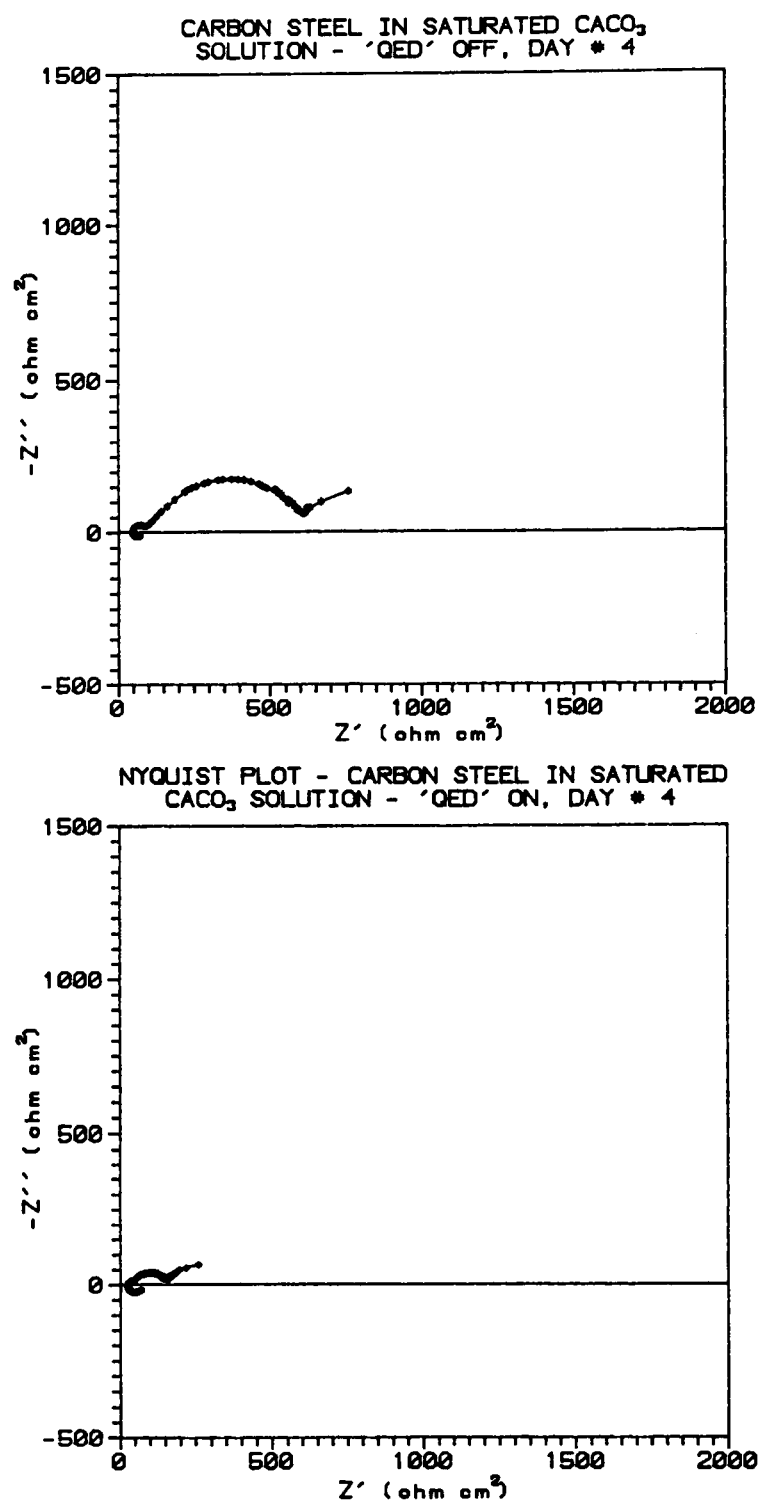


Figure 4.7 Complex plane plots for specimens under control and test conditions after day 4.

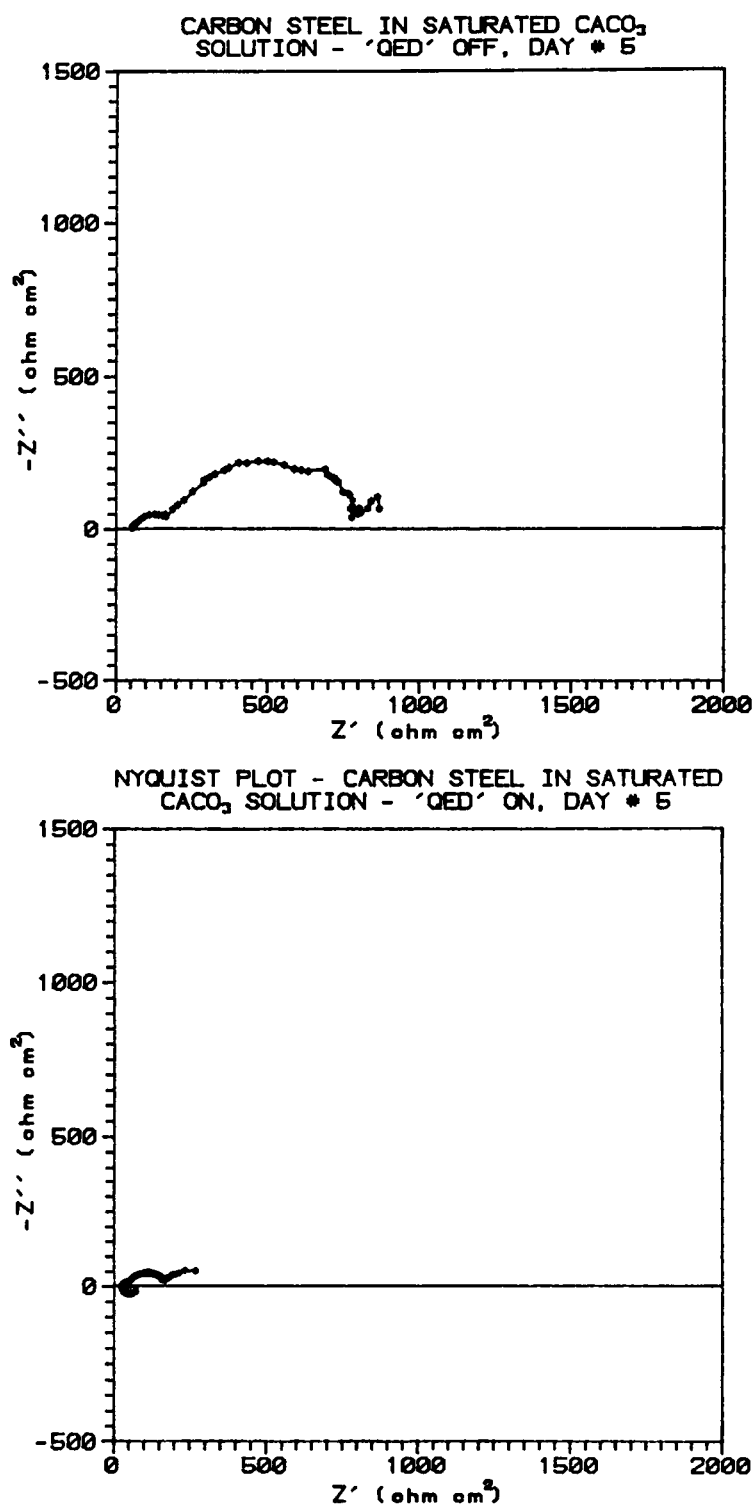


Figure 4.8 Complex plane plots for specimens under control and test conditions after day 5.

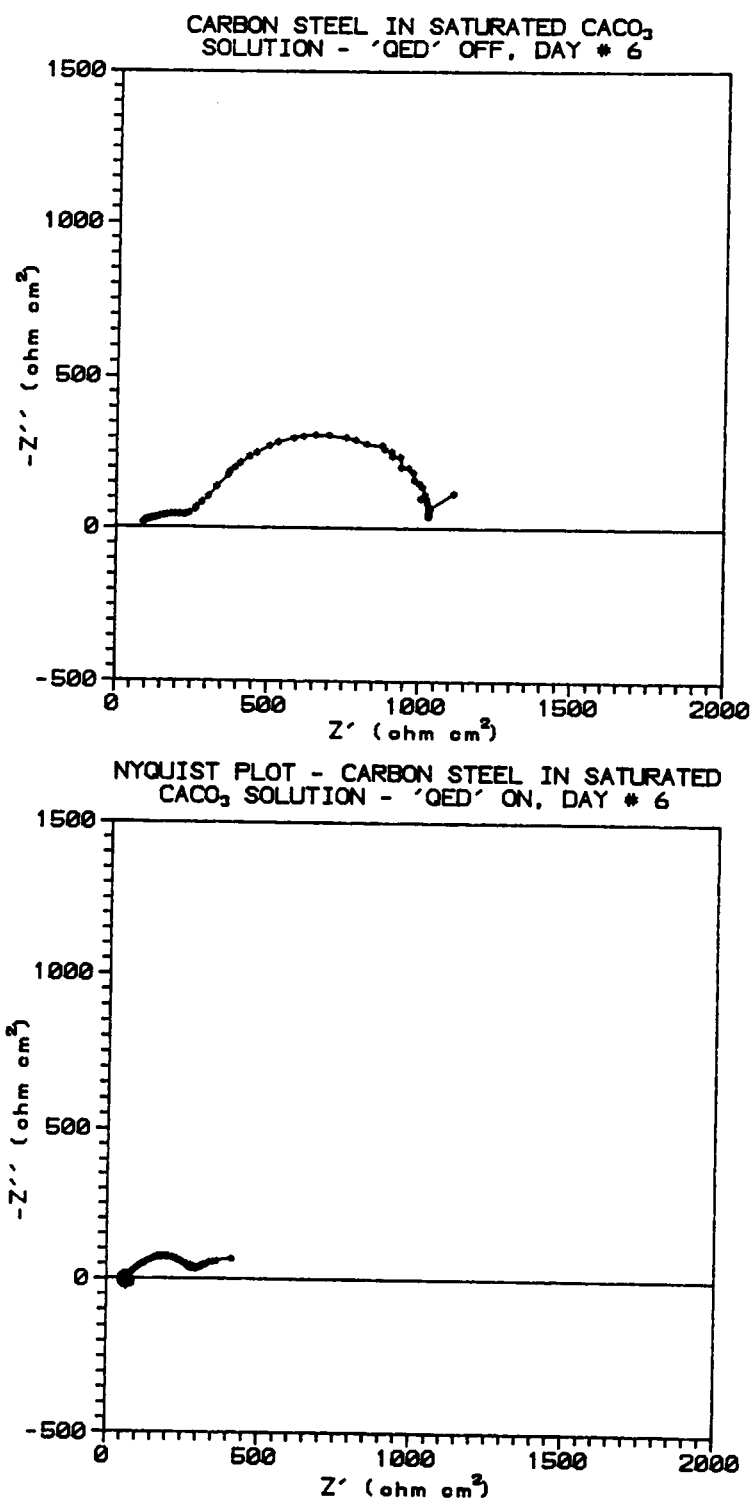


Figure 4.9 Complex plane plots for specimens under control and test conditions after day 6.

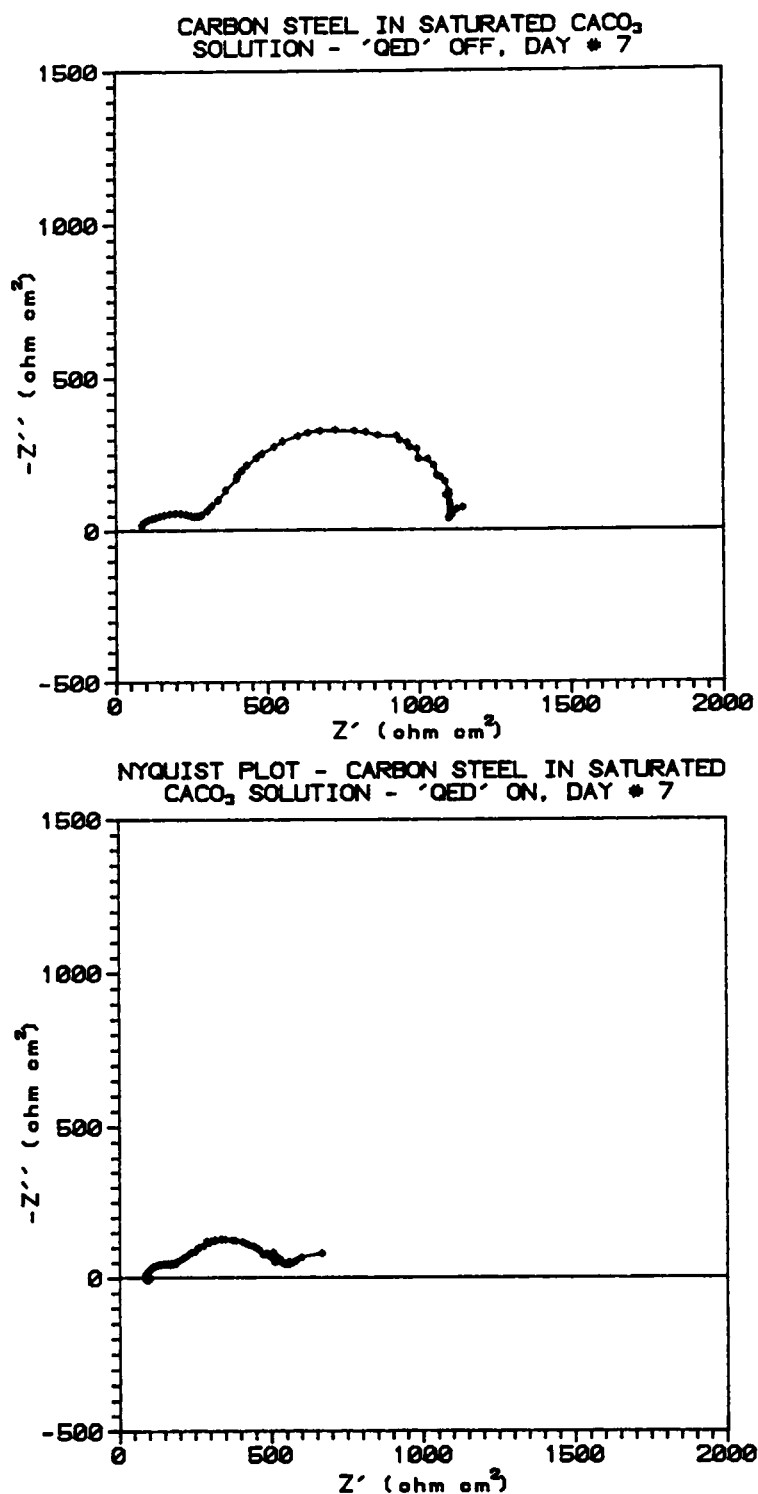


Figure 4.10 Complex plane plots for specimens under control and test conditions after day 7.

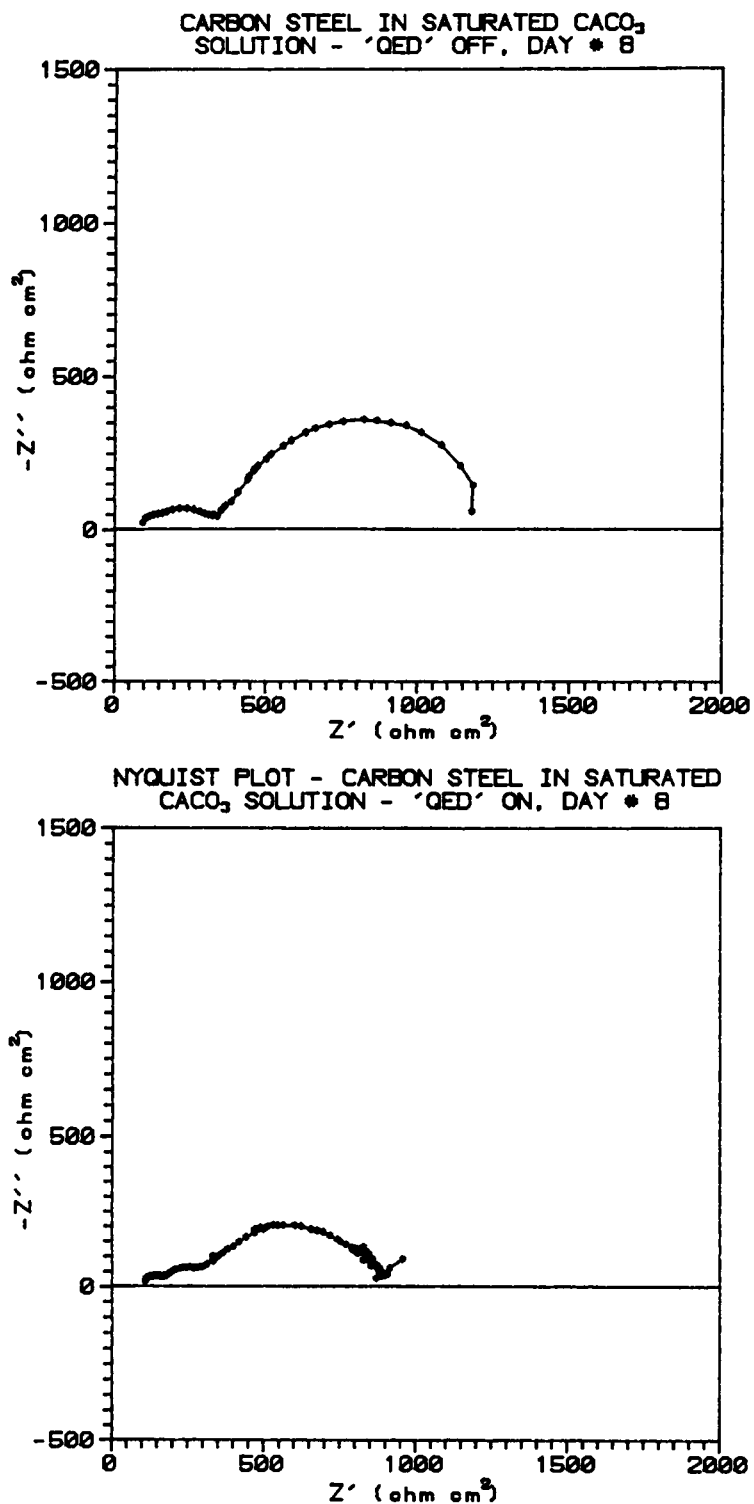


Figure 4.11 Complex plane plots for specimens under control and test conditions after day 8.

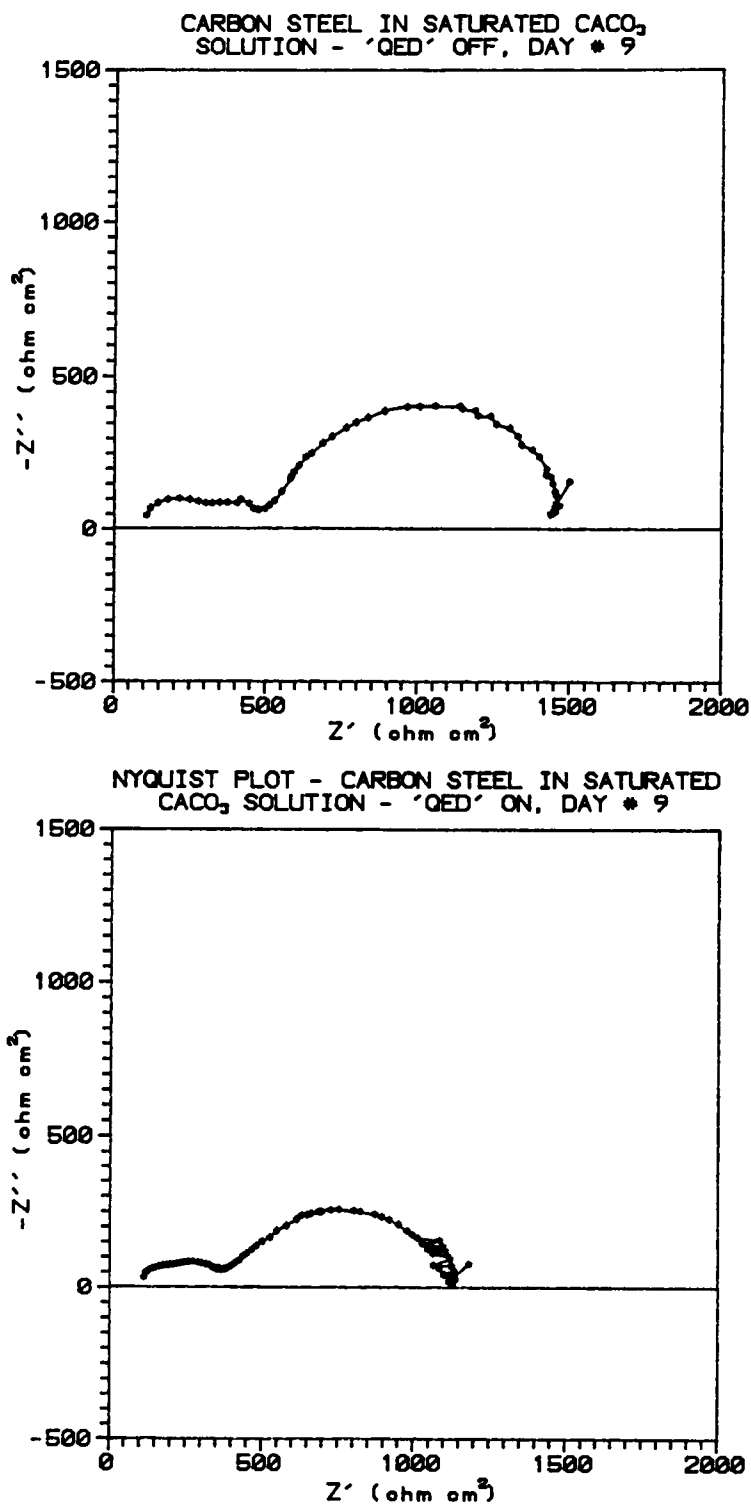


Figure 4.12 Complex plane plots for specimens under control and test conditions after day 9.

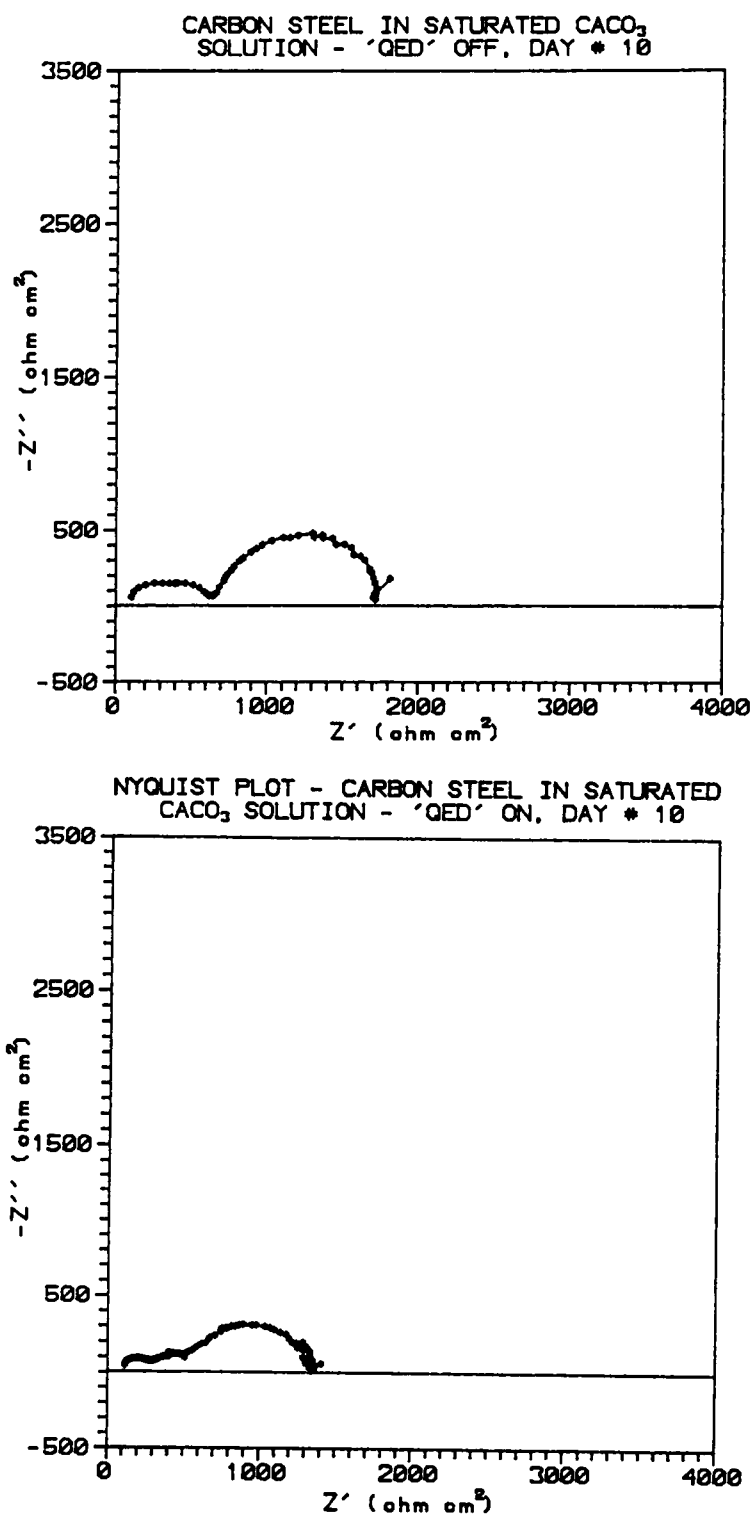


Figure 4.13 Complex plane plots for specimens under control and test conditions after day 10.

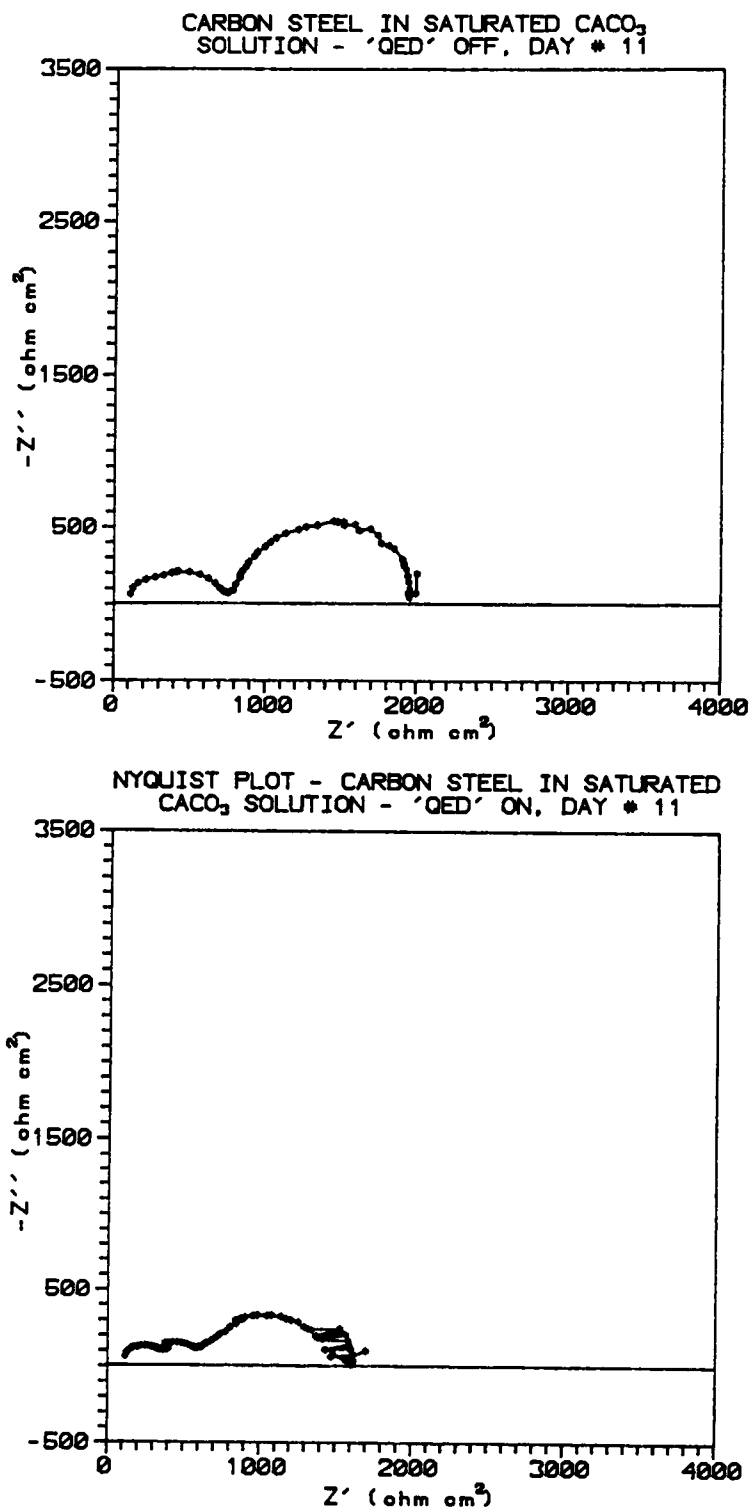


Figure 4.14 Complex plane plots for specimens under control and test conditions after day 11.

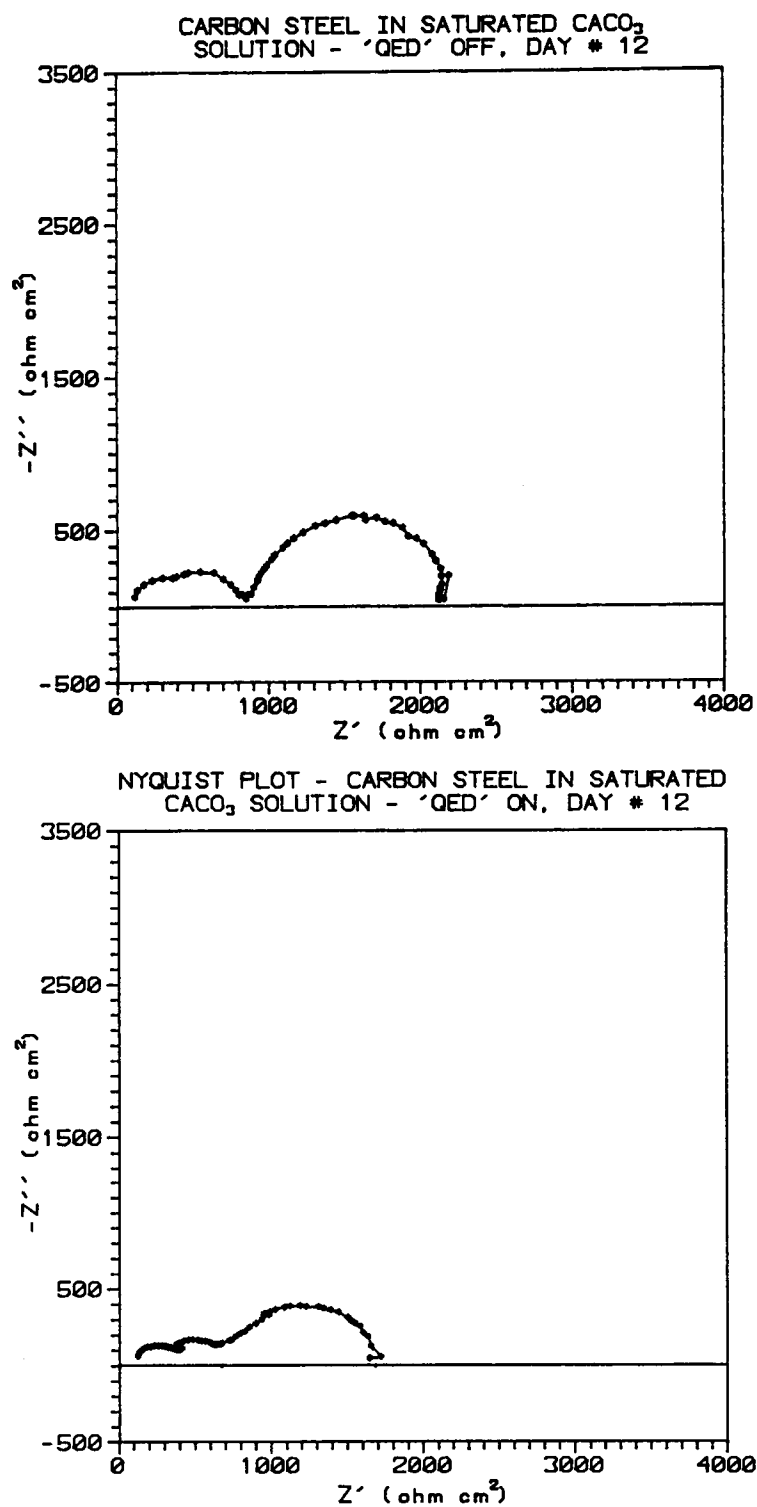


Figure 4.15 Complex plane plots for specimens under control and test conditions after day 12.

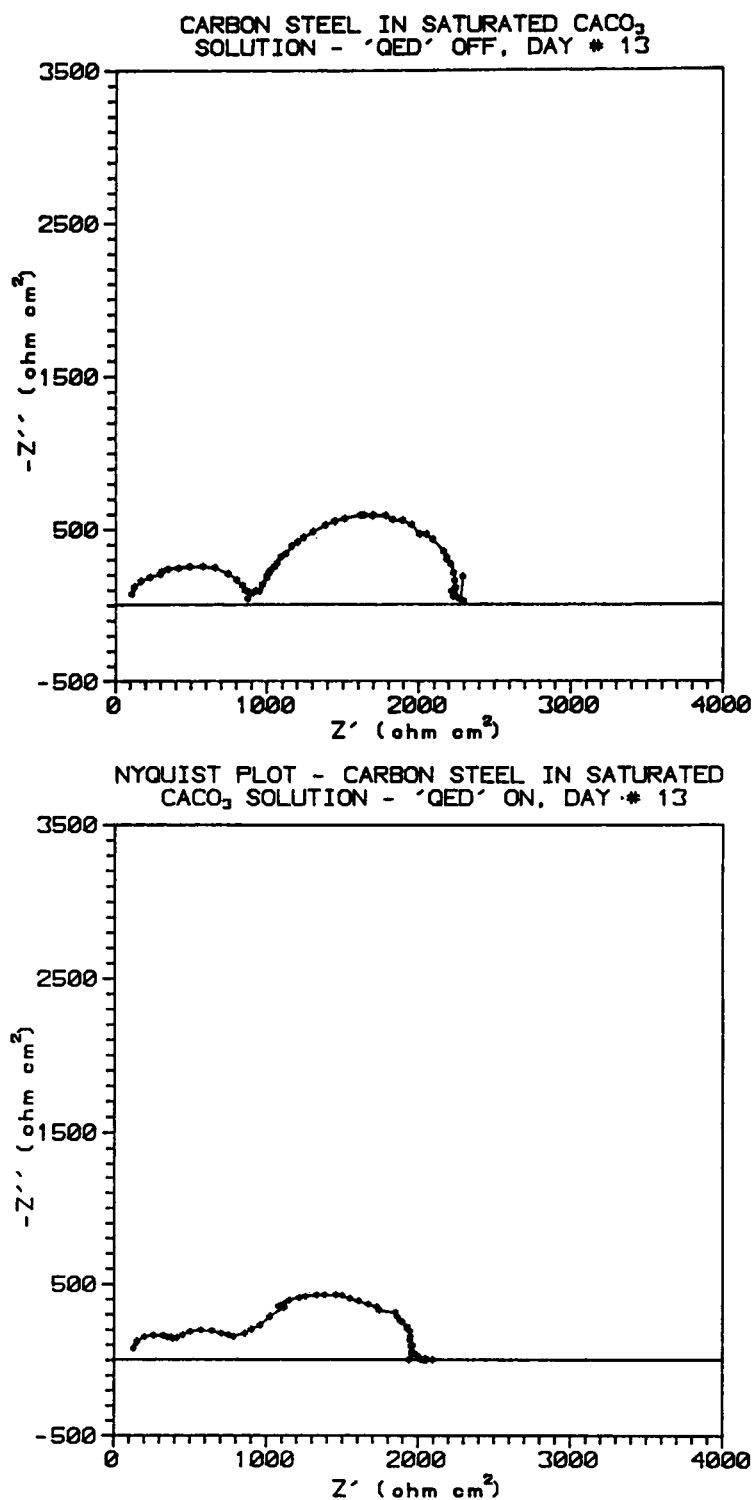


Figure 4.16 Complex plane plots for specimens under control and test conditions after day 13.

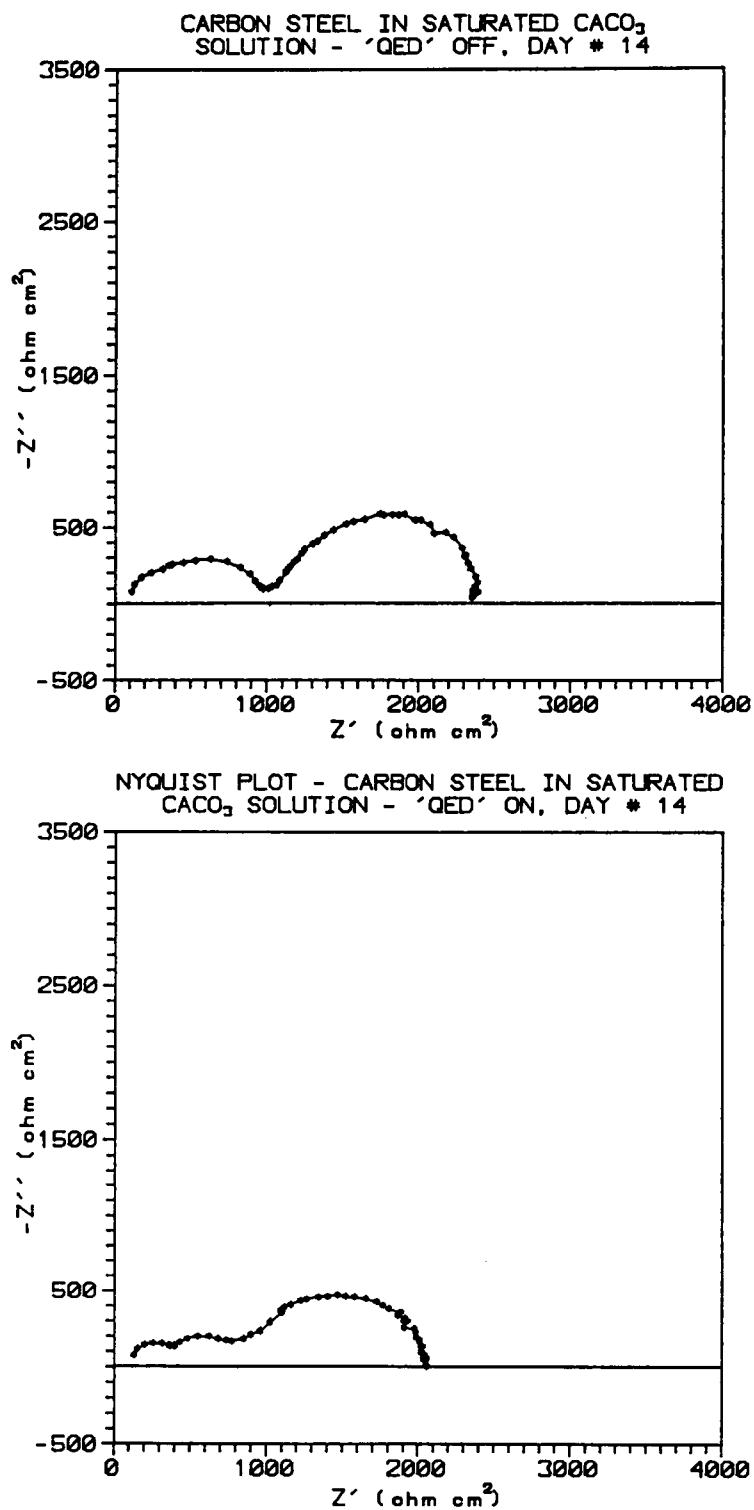


Figure 4.17 Complex plane plots for specimens under control and test conditions after day 14.

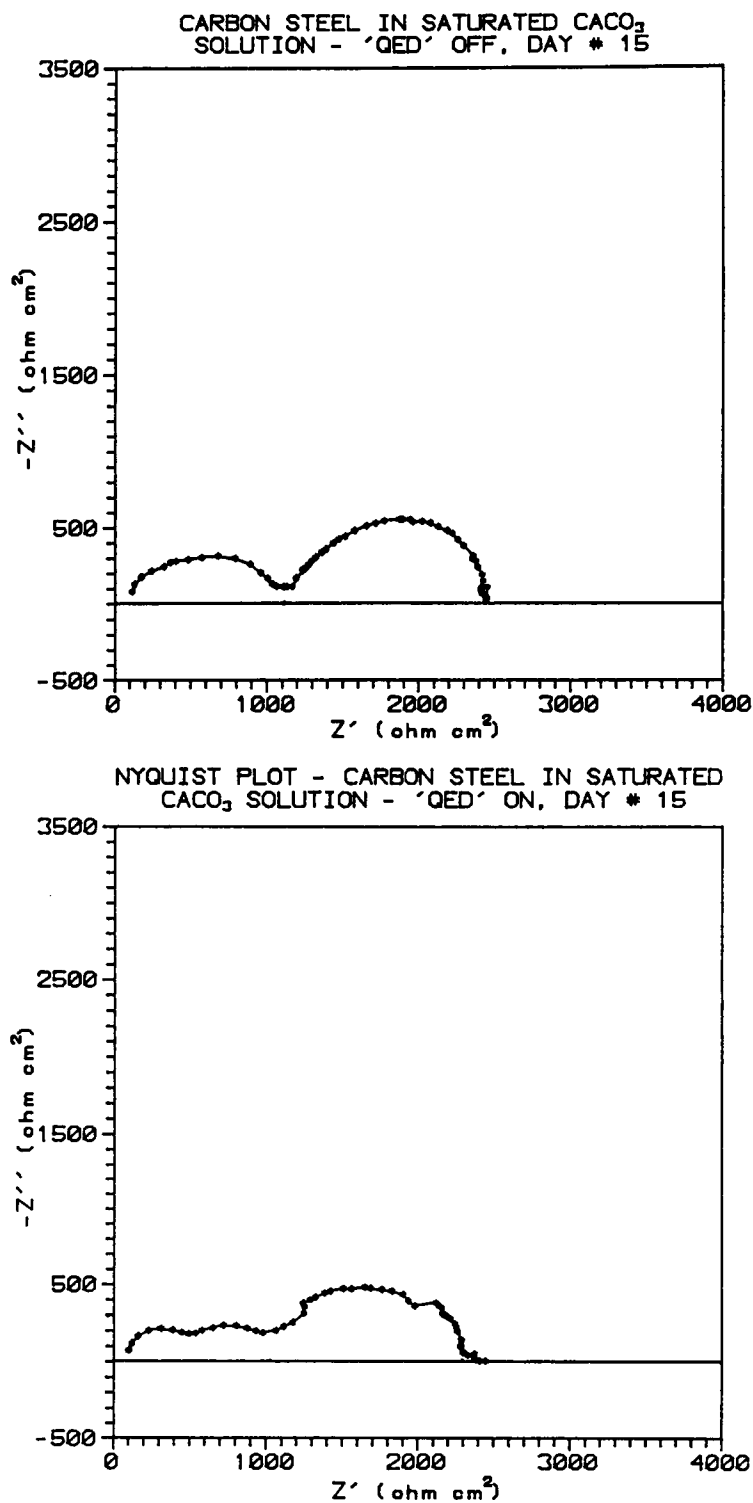


Figure 4.18 Complex plane plots for specimens under control and test conditions after day 15.

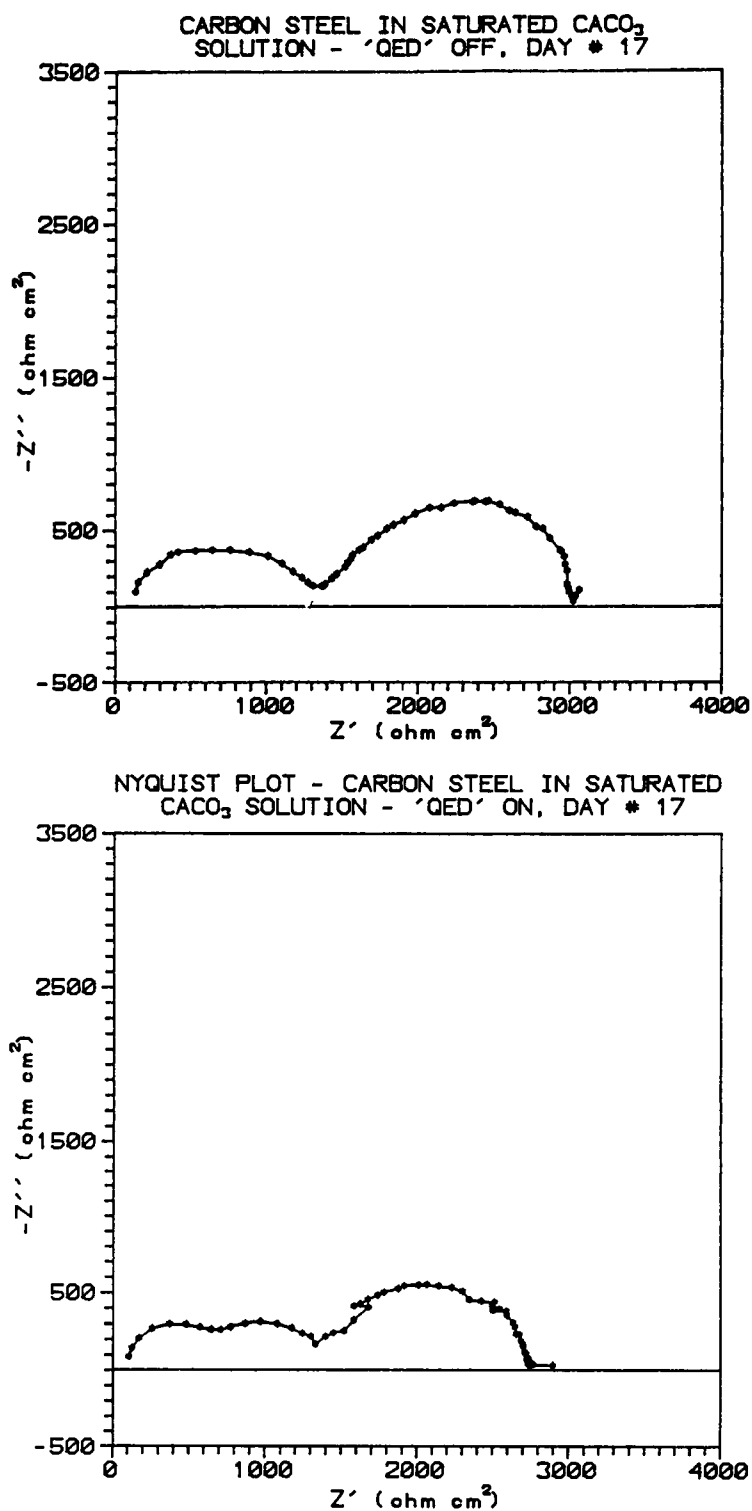


Figure 4.19 Complex plane plots for specimens under control and test conditions after day 17.

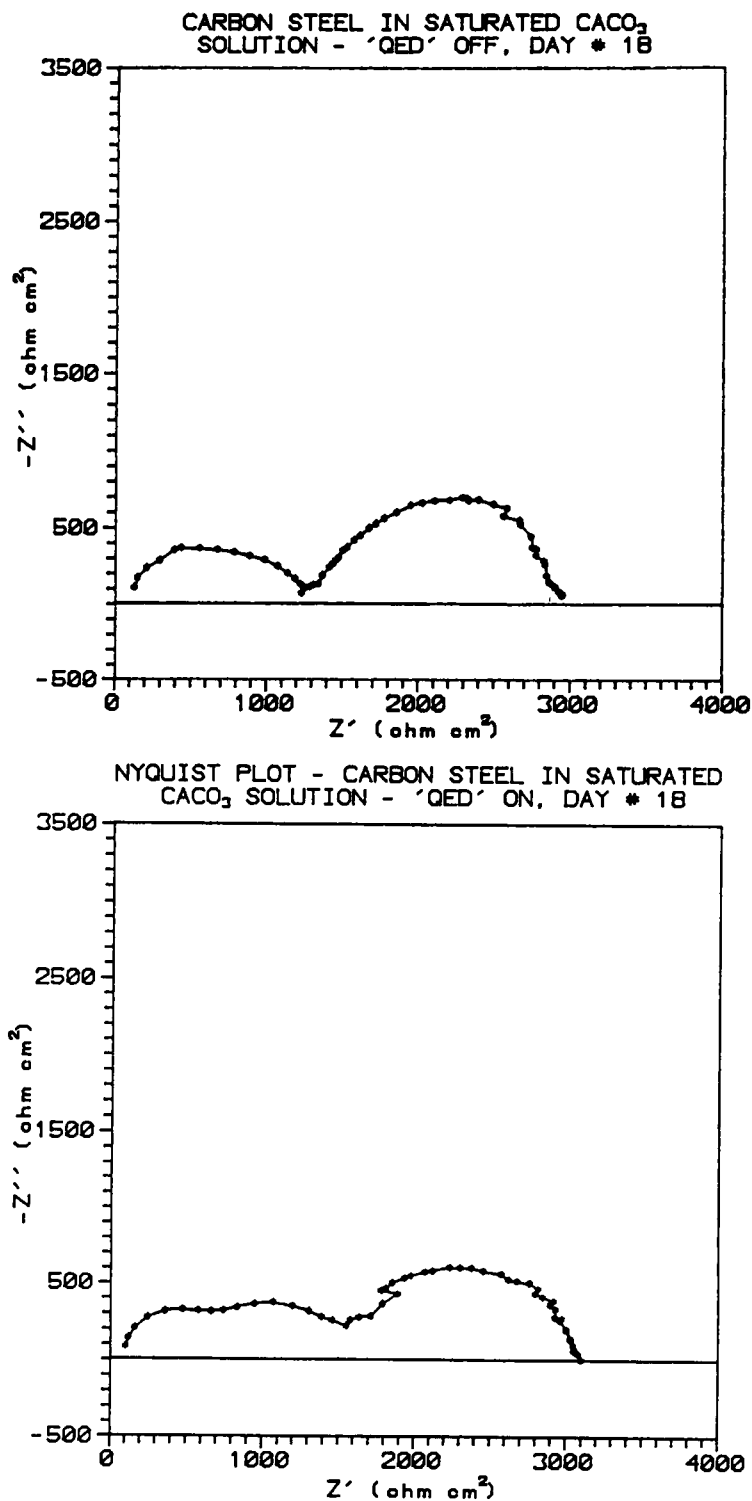


Figure 4.20 Complex plane plots for specimens under control and test conditions after day 18.

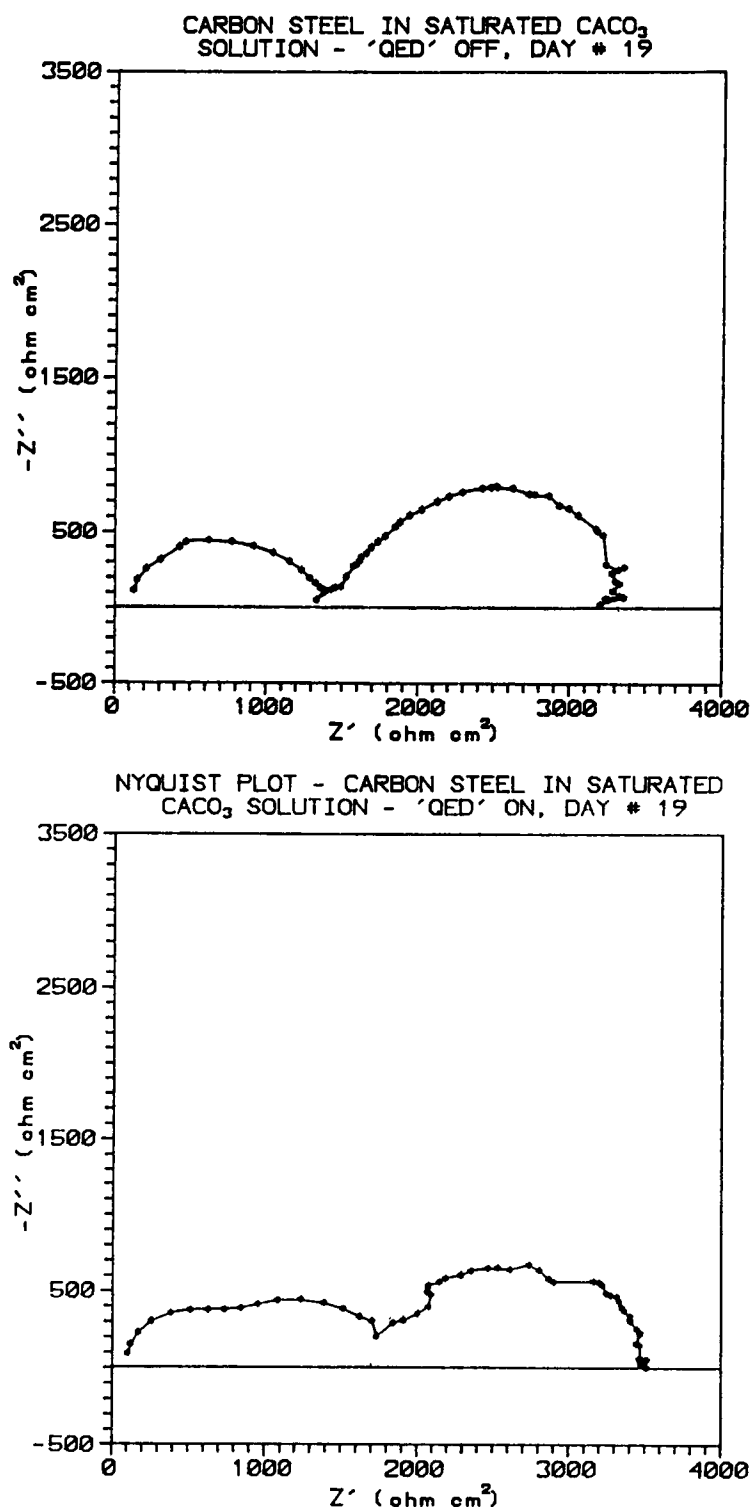


Figure 4.21 Complex plane plots for specimens under control and test conditions after day 19.

Careful observation of this plot showed a very small semicircle in the high frequency region. The presence of this semicircle indicated a completely resolved second relaxation phenomenon. The plot obtained on the fourth day showed this second semicircle clearly in the high frequency region.

The complex plane plots obtained during days 6 through 10 showed a more resolved low frequency semicircle with its center almost on the Z' axis. Another trend to be noted was the increase in the diameter of both the low frequency and high frequency semicircles. It should be noted, however, that during this time period, the high frequency semicircle had a flattened top. Similar trends were seen in the plots obtained during days 11 through 19. It can be seen from these plots that the flattened top of the high frequency semicircle had become less pronounced with time. At the end of the nineteenth day, the plot obtained showed two semicircles both flattened to a certain extent. The semicircle at high frequency seemed to be flattened more than the semicircle at low frequency. Even though it is not very clear, it appeared that the low frequency semicircle in the plots obtained during days 8 through 12 was a combination of two small partially resolved semicircles.

The following mechanism is proposed for the origin of the impedance spectra observed under control conditions. It is believed that during the first 1 or 2 days, corrosion of the metal surface was the predominant process, taking place on the surface of the specimen. During this period, there was formation of a layer of

corrosion products (iron oxides, hydroxides, and carbonates) on the metal surface. This porous layer of corrosion products provided nucleation sites for the precipitation of calcium carbonate in the formation of scale. The precipitation of the calcium carbonate as a clear-cut porous scale layer, on top of the corrosion products must have started in the vicinity of the third day. These phenomena explain the sudden appearance of a second semicircle in the high frequency region.

Once a thin porous layer of scale was formed, it further grew in a direction perpendicular to the surface of the specimen. The growth of the scale layer must have led to a decrease in the rate of the corrosion reaction. This explains the increase in the diameter of the low frequency semicircle. The difference between the low frequency and the high frequency intercepts of the low frequency semicircle gives the polarization resistance. Further, it is believed that as the scale layer grew in thickness, the average pore size in the scale layer decreased. The pores could also have been partially blocked by the some of the corrosion products at the metal/electrolyte interface in the pores. Both these factors must have led to an increase in the pore resistance. These phenomena explain the increase in the diameter of the high frequency semicircle which represents the pore resistance. The pore resistance is the difference between the low frequency and high frequency intercepts of the high frequency semicircle. A schematic representation of the proposed corrosion product and scale layers on the metal surface is shown in Figure 4.22. The above mechanism proposed can be modeled by the equivalent circuit

shown in Figure 4.23. From the complex plane plots it is quite obvious that there are two circuit elements contributing to the impedance of the system. In this figure R_{pO} represents the pore resistance, C_s represents the scale layer capacitance, R_Ω represents the uncompensated resistance, R_p represents the polarization resistance, and C_{dl} represents the double layer capacitance at the metal/electrolyte interface. Figure 4.24 shows a Nyquist plot for the equivalent circuit shown in Figure 4.23. In the complex plane plots, the high frequency semicircle represents the double layer capacitance in parallel with the polarization resistance. The low frequency intercept of the low frequency semicircle represents the sum of R_Ω , R_{pO} , and R_p . The sum of R_Ω and R_{pO} is in the vicinity of the intersection of the two semicircles. R_Ω is given by the high frequency intercept of the high frequency semicircle.

In general, the porous scale layer on a metal may be considered to be analogous to a passive surface containing corrosion pits. The pores in the scale layer can be considered to be artificial pits. Models similar to the equivalent circuit shown in Figure 4.23 were suggested for the latter case by other investigators[21,22]. The mechanism proposed in the previous paragraphs is simply the inverse case of the deterioration of an organic coating or layer applied to a metal surface. The slow deterioration of the coating leads to formation of pores, thereby increasing the corrosion rate. Models similar to the equivalent circuit shown in Figure 4.23 were suggested for the case of a deteriorating organic coating on a metal surface[23, 24]. The case of the formation of a scale layer on a bare

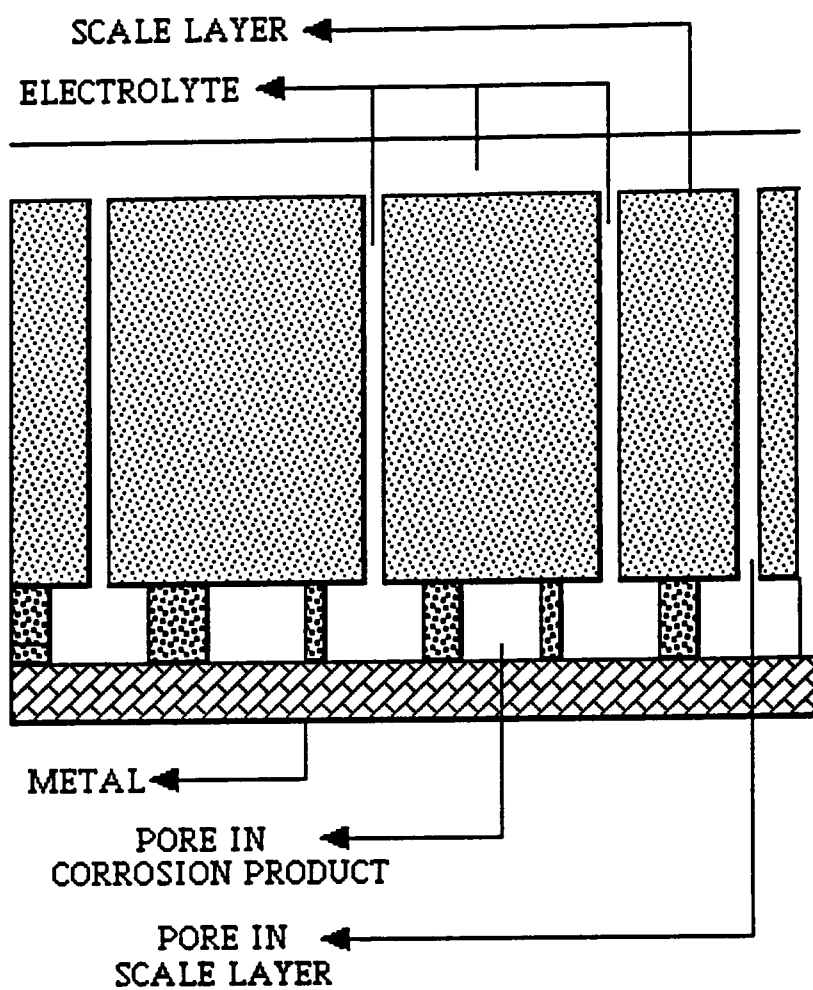


Figure 4.22 Schematic representation of the model proposed for scale and corrosion product layers on the metal surface.

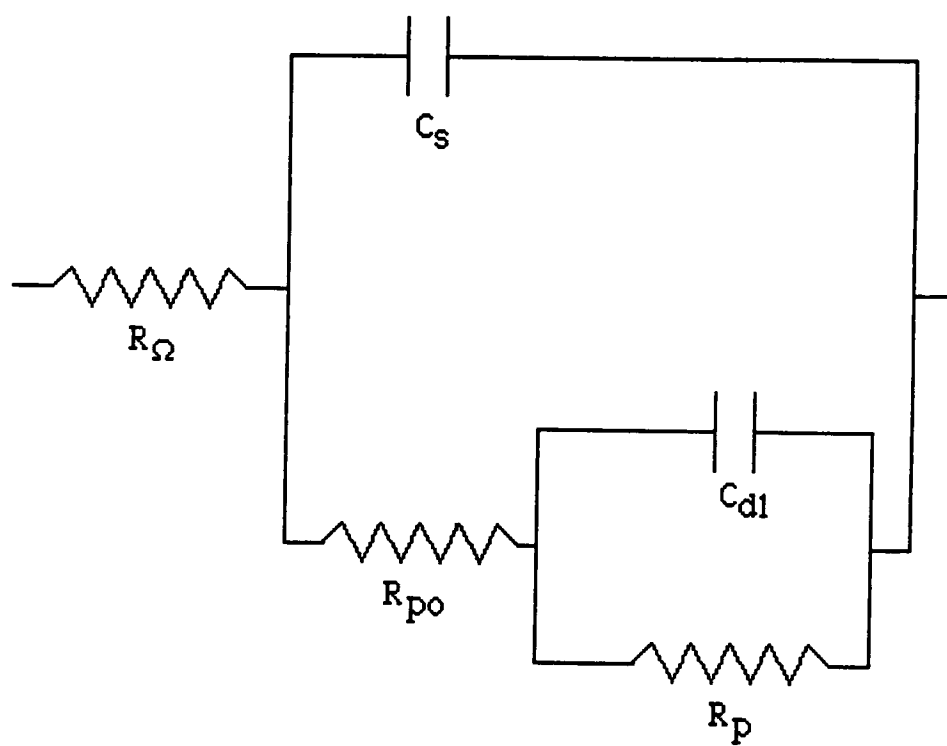


Figure 4.23 Sketch of the equivalent circuit for the model proposed.

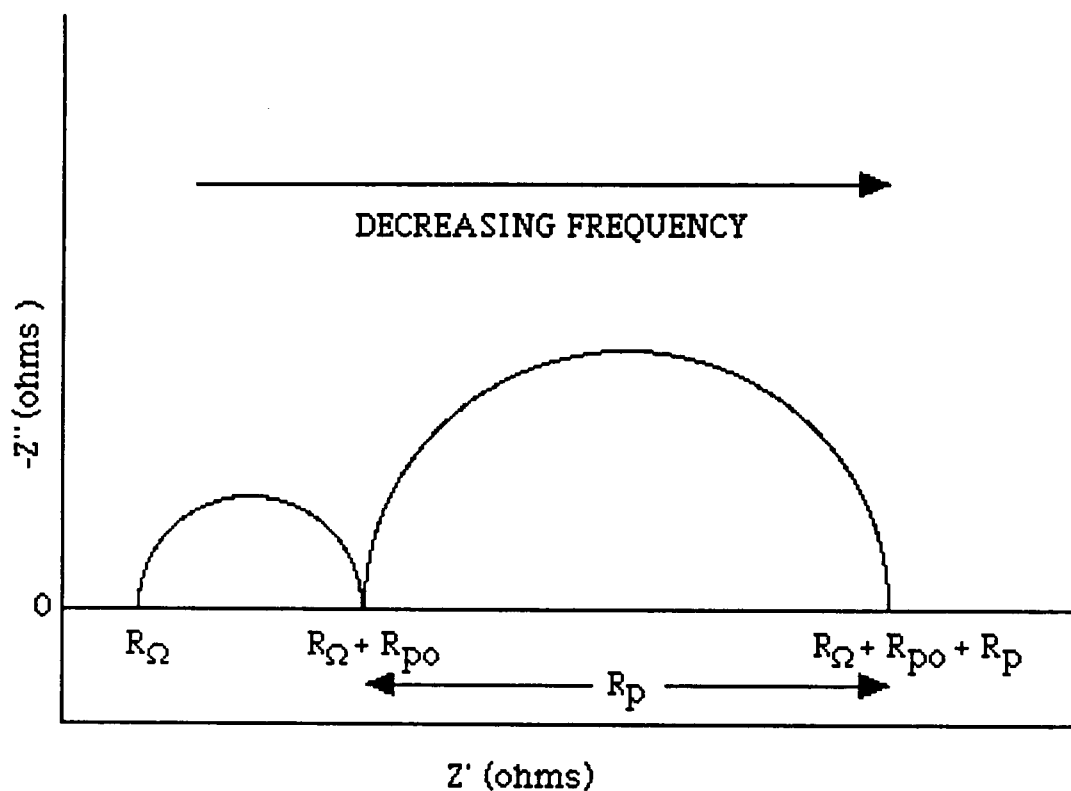


Figure 4.24 Schematic complex plane plot of proposed corrosion-product/scale distribution (Figure 4.22) and resultant equivalent diagram (Figure 4.23).

metal surface, and the case of the deterioration of an organic coating on a metal surface, start from opposite extremes. But after some time, both these cases reach the same stage where a porous layer covers the metal surface. Finally, the former case reaches a stage where the pore resistance tends to infinity, whereas the latter case reaches a stage where the pore resistance tends to zero. These observations further strengthen the mechanism proposed.

In the case of the specimen in the test medium under test conditions (QED activated), some of the major trends mentioned above were seen in the complex plane plots. But these trends occurred with a time lag. For example, the trends which were seen in the specimen under control conditions on the third day were seen in the specimen under test conditions on the sixth day. The trend being referred to is the appearance of the second semicircle in the high frequency region. Another major difference seen in the complex plane plots for the two cases was the appearance of two clearly visible partially resolved semicircles in the high frequency region for the specimen under test conditions. This condition seemed to be more prominent in the plots obtained during days 8 to 15.

The time lag in showing similar trends, and the appearance of two semicircles in the high frequency region were attributed to the RF treatment of the test medium.

The time lag in showing similar trends is believed to be due to RF treatment slowing down the scale formation. The appearance of two partially resolved semicircles in the high frequency region is

explained as follows. The scale formation must have slowed down due to the RF treatment. As a result, the layer of scale on the corrosion product must have been extremely thin and very porous. This probably resulted in alternate porous layers of scale, corrosion product, and scale. Apparently, one of the partially resolved semicircles is due to the corrosion product layer. The effect of the corrosion product layer must have been magnified by the presence of thin layers of scale above and below it. With the passage of time a considerably thick layer of scale must have formed on top. As it grew this comparatively thick layer of scale must have slowly suppressed the effect of the sandwiched corrosion product layer. As a result, it can be seen that with the passage of time the two semicircles combined to form a depressed single semicircle.

The above proposed mechanism explains the appearance of two semicircles in the high frequency region. In a sense, the two semicircles appeared because the scale formation was slow. This fact indicated that the RF treatment does slow down the formation of scale.

To make sure that the mechanism proposed above was indeed correct, a carbon steel specimen was exposed to tap water with pH adjusted to 8.5. The pH of the tap water was monitored throughout the period of exposure and was found to be constant. The complex plane plots are shown in Figures 4.25 through 4.33. These complex plane plots showed more or less depressed, partially or completely resolved semicircles. There was no indication of a second semicircle

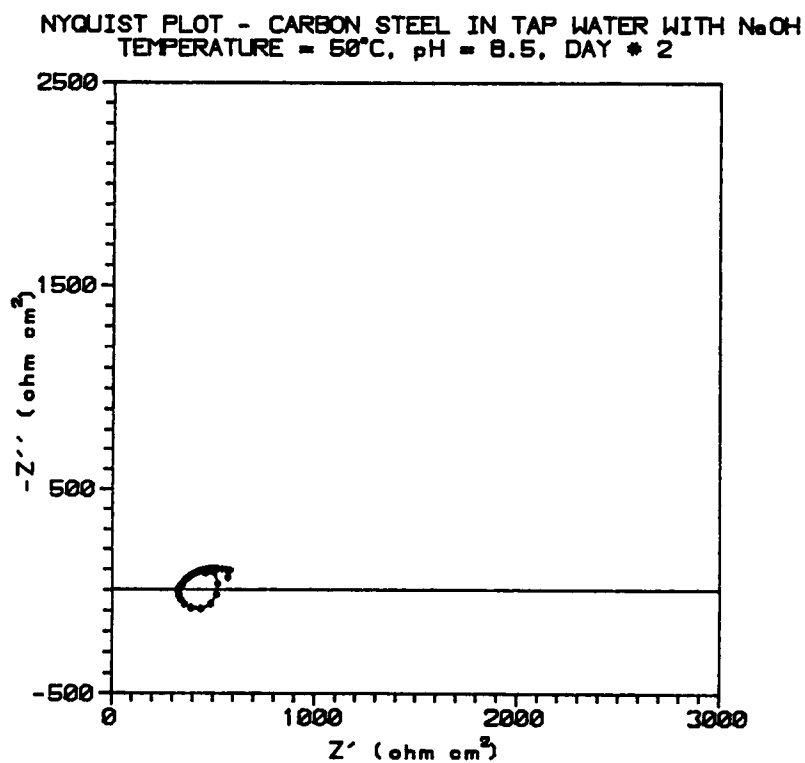
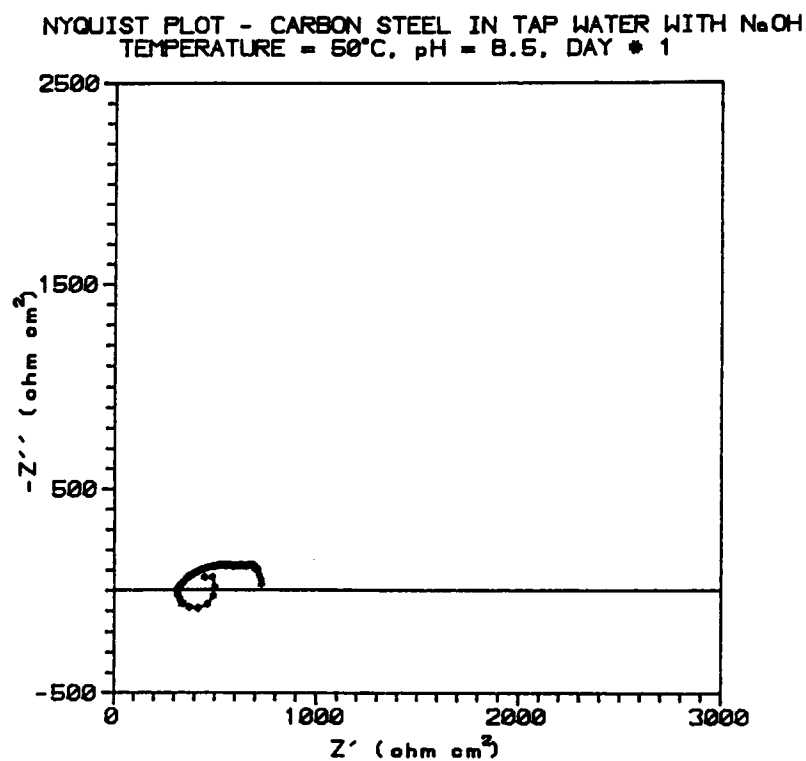


Figure 4.25 Complex plane plots for specimen in tap water after days 1 and 2.

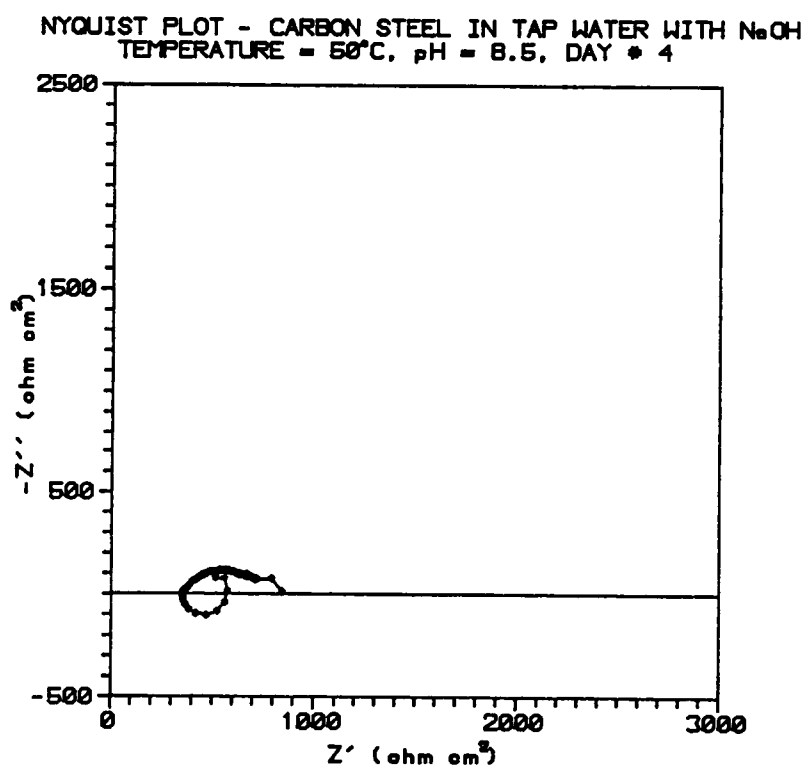
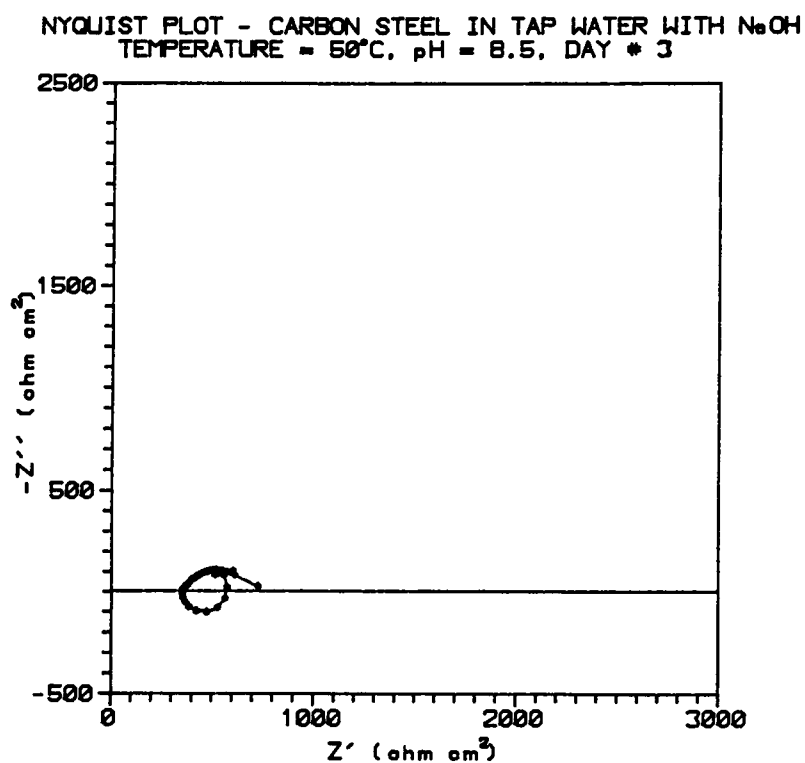


Figure 4.26 Complex plane plots for specimen in tap water after days 3 and 4.

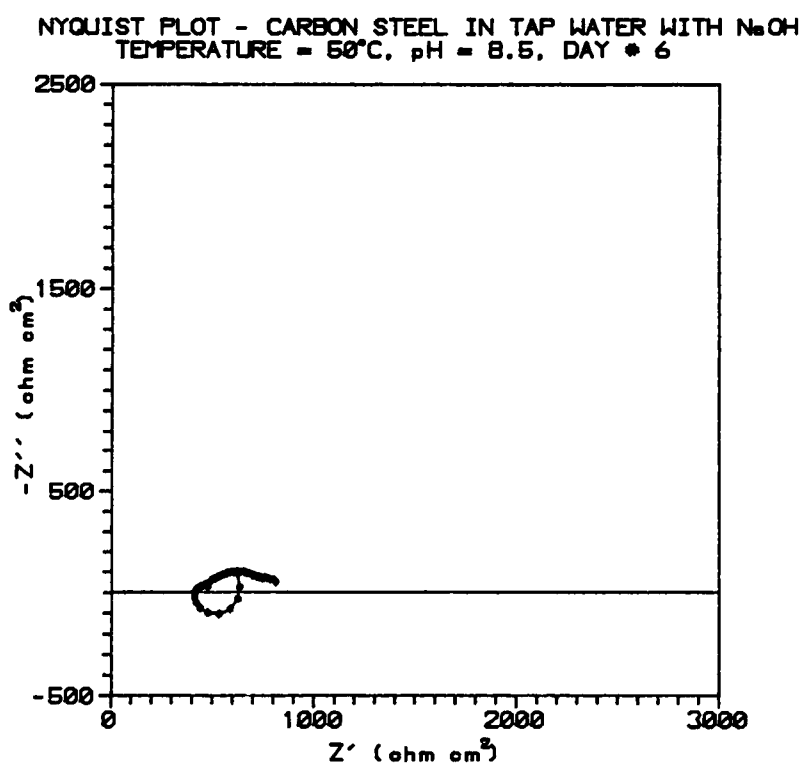
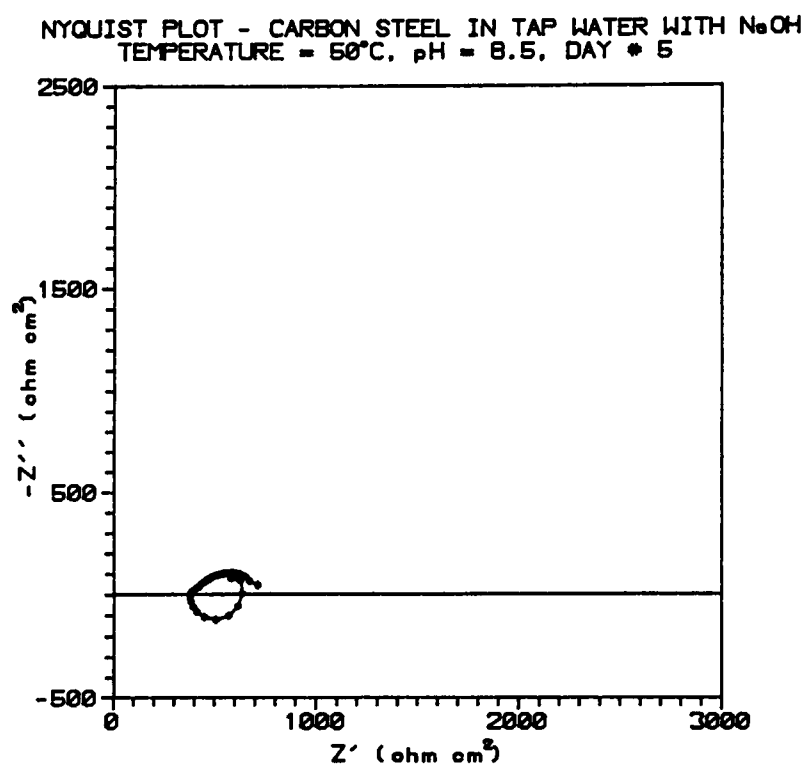
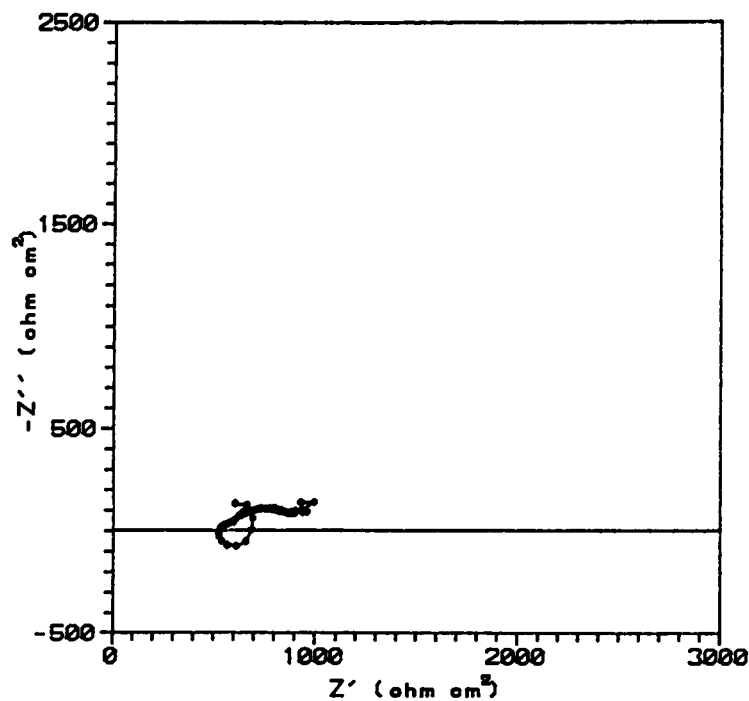


Figure 4.27 Complex plane plots for specimen in tap water after days 5 and 6.

NYQUIST PLOT - CARBON STEEL IN TAP WATER WITH NaOH
TEMPERATURE = 50°C, pH = 8.5, DAY # 7



NYQUIST PLOT - CARBON STEEL IN TAP WATER WITH NaOH
TEMPERATURE = 50°C, pH = 8.5, DAY # 8

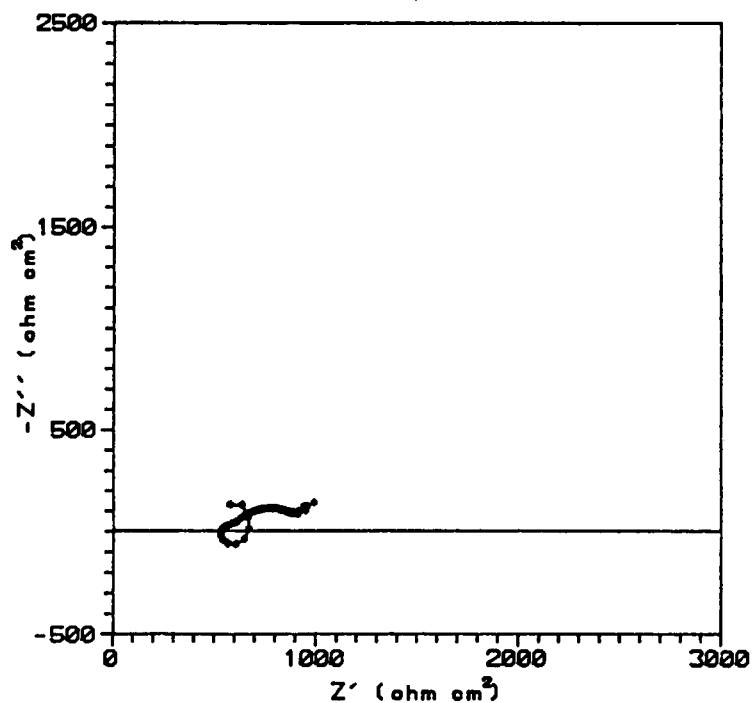


Figure 4.28 Complex plane plots for specimen in tap water after days 7 and 8.

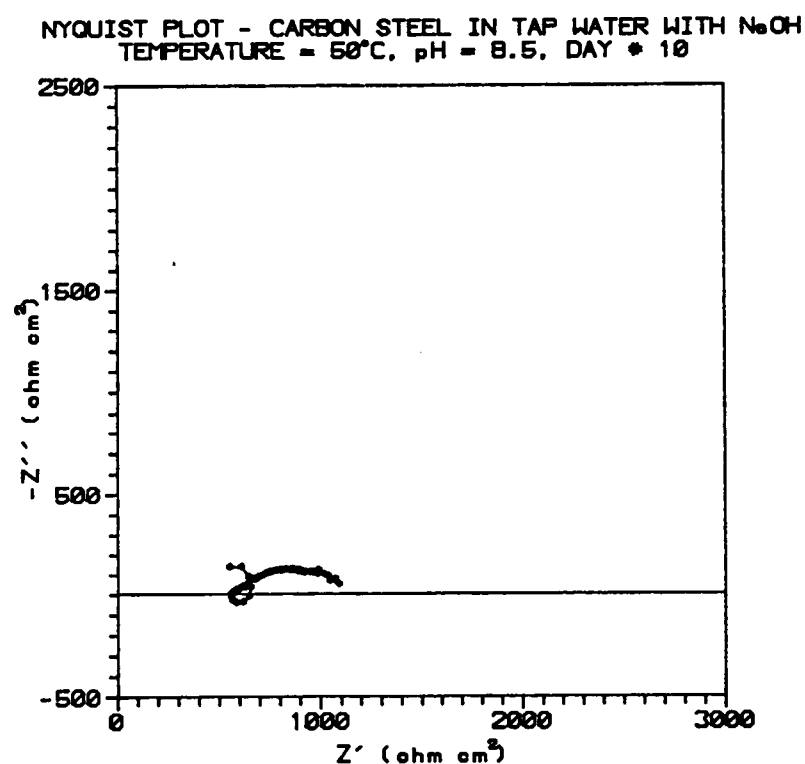
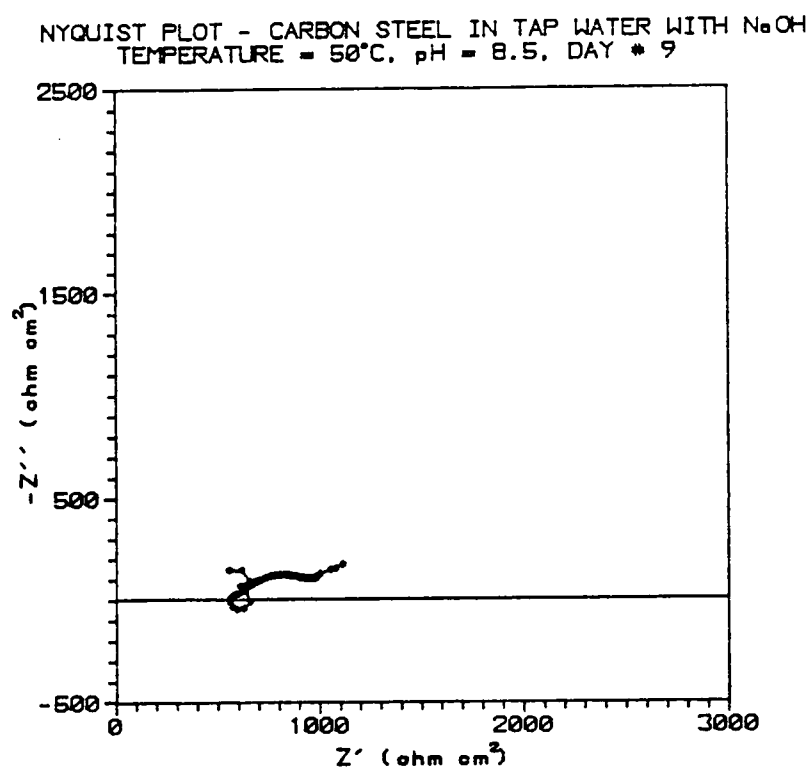


Figure 4.29 Complex plane plots for specimen in tap water after days 9 and 10.

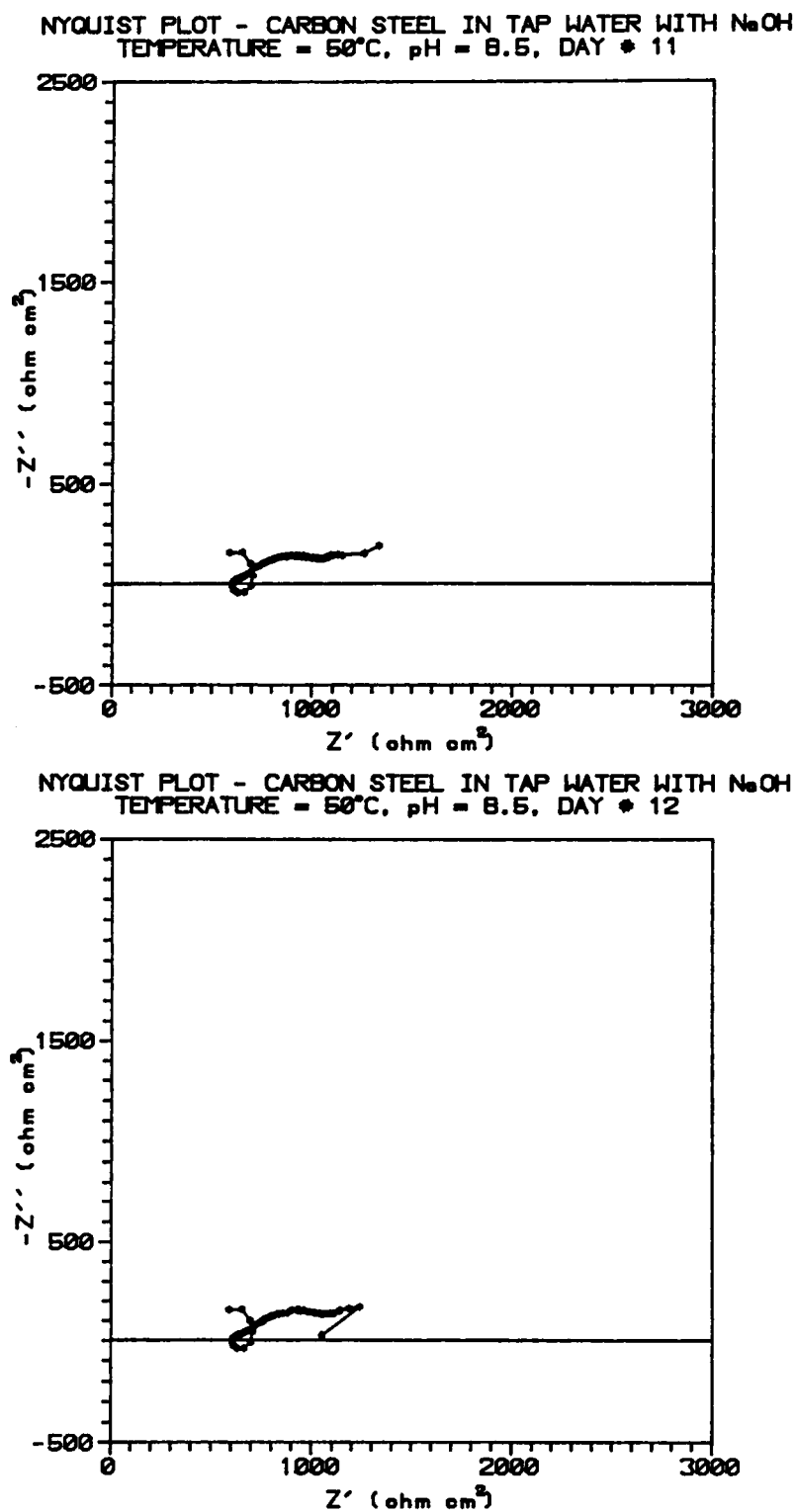


Figure 4.30 Complex plane plots for specimen in tap water after days 11 and 12.

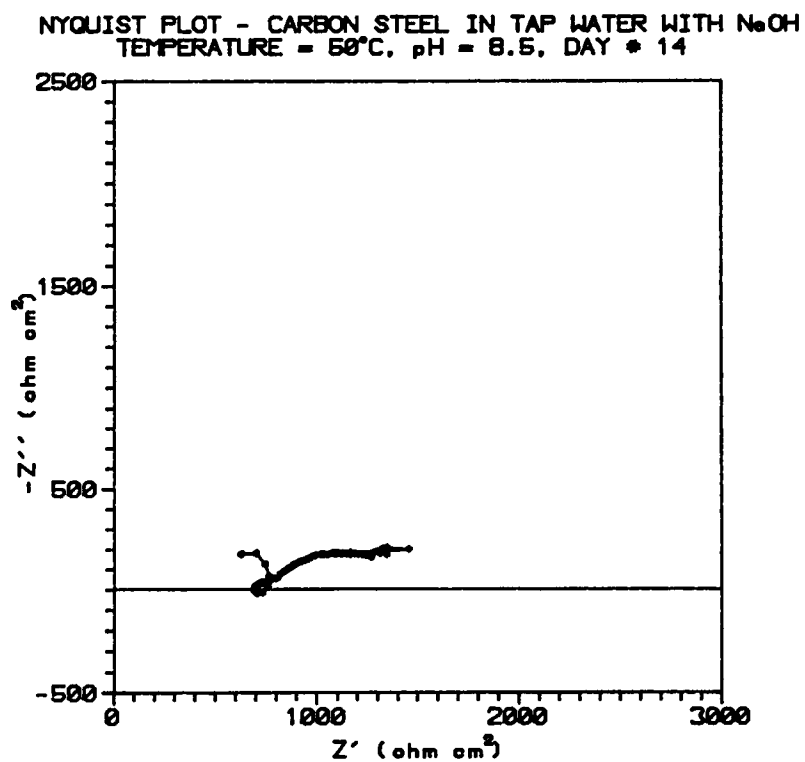
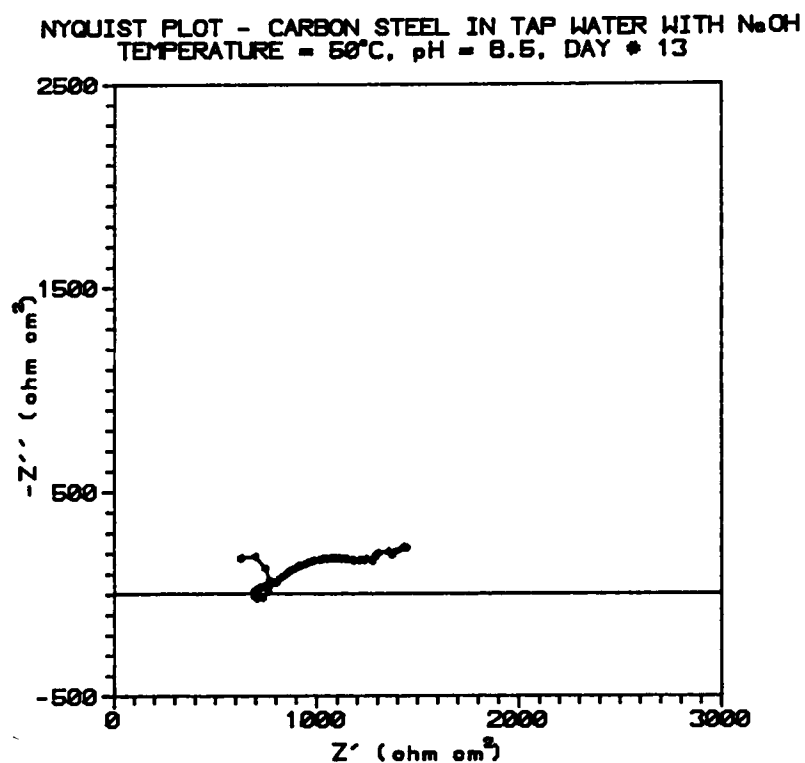


Figure 4.31 Complex plane plots for specimen in tap water after days 13 and 14.

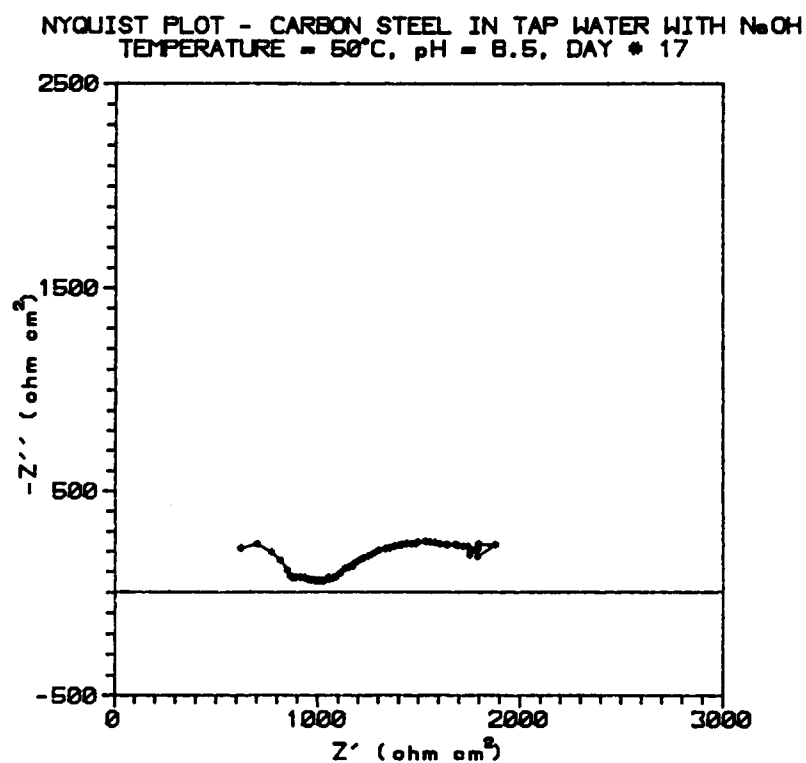
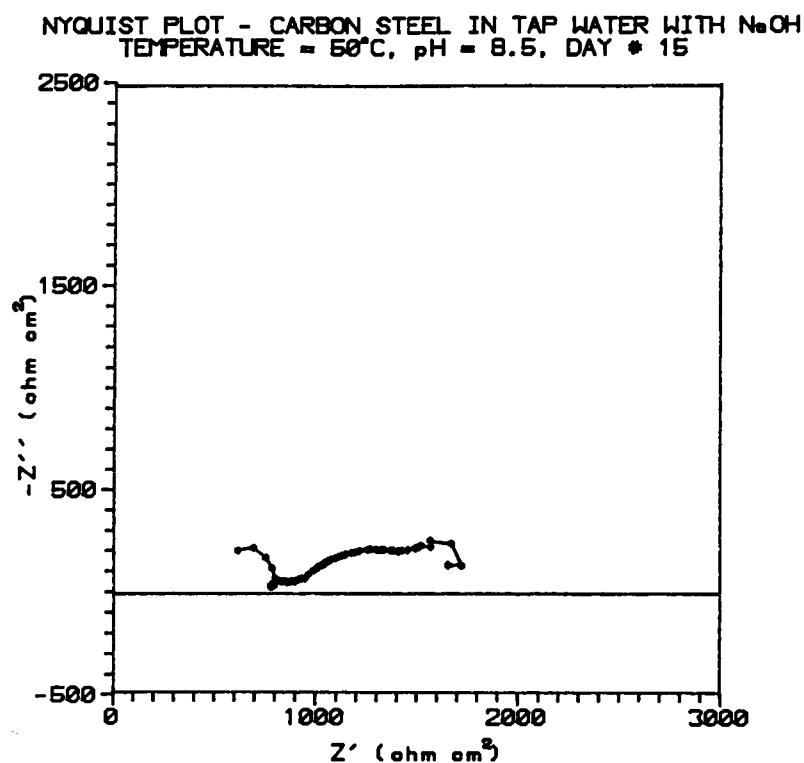


Figure 4.32 Complex plane plots for specimen in tap water after days 15 and 17.

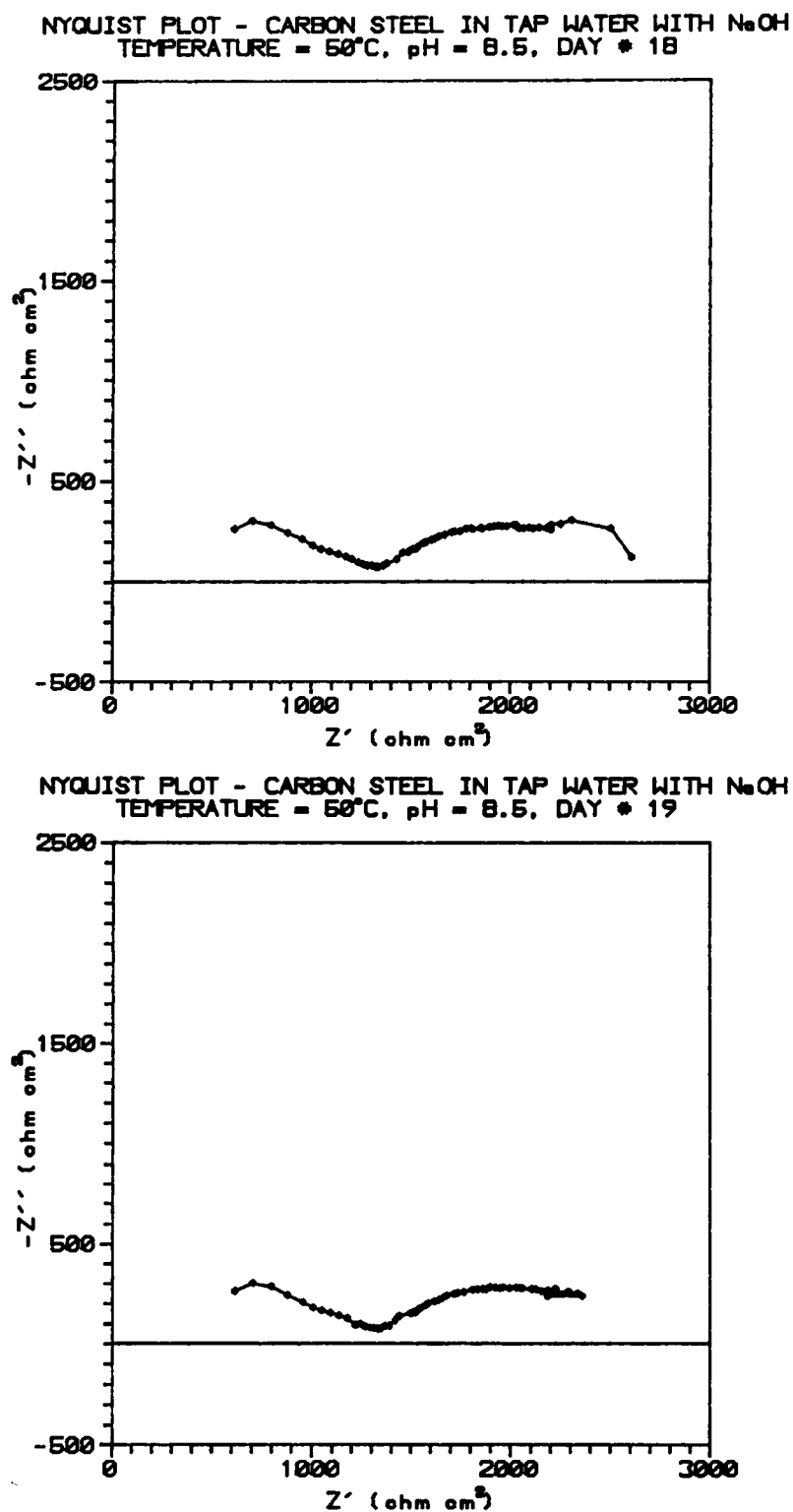


Figure 4.33 Complex plane plots for specimen in tap water after days 18 and 19.

in any of the plots. Again, the negative values of impedance in the initial period, and the high frequency loop in the latter period were because of the phase shift arising from the potentiostat. In this case, the negative loop obtained was much larger than the negative loops obtained in the cases of specimens exposed to the test medium. This was probably due to a larger difference between the impedance of the system and the measuring resistor of the potentiostat compared to the cases of specimens exposed to the test medium. The complex plane plots obtained represented a simple corroding surface, and can be modeled by the simple equivalent circuit shown in Figure 2.6. Thus, the absence of a second semicircle in the complex plane plots indicated that the corrosion product by itself did not influence the impedance spectra. These results provided additional credibility to the mechanism proposed and strengthened the argument that RF treatment slows down scale formation.

The polarization resistance data obtained from the impedance spectra in all three cases are given in Table 2. In all cases, the polarization resistance (R_p) was determined as the diameter of the lowest frequency semicircle. The corrosion rates obtained from the polarization data are also shown in Table 2. To obtain these corrosion rates, first the corrosion current densities (i_{CORR}) were calculated from Equation 2.21. Then the corrosion penetration rates (CPR) in mils per year (mpy) were calculated from Equation 2.22. In the calculations of i_{CORR} from Equation 2.21, the value of 0.026 V was chosen for the expression

Table 2. Polarization Resistance Values Obtained From Impedance Spectra Along With Calculated Corrosion Rates

DAY	R _p - QED OFF (ohm cm ²)	CPR - QED OFF (mpy)	R _p - QED ON (ohm cm ²)	CPR - QED ON (mpy)	R _p - TAP WATER (ohm cm ²)	CPR - TAP WATER (mpy)
1	292	40.92	276	43.29	390	30.64
2	276	43.29	236	50.63	305	39.17
3	423	28.25	171	69.87	317	37.69
4	561	21.30	138	86.58	415	28.79
5	642	18.61	146	81.84	354	33.75
6	789	15.14	252	47.41	366	32.65
7	813	14.70	374	31.95	402	29.72
8	862	13.86	545	21.92	390	30.64
9	951	12.56	707	16.90	427	27.98
10	1106	10.80	878	13.61	512	23.34
11	1203	9.93	927	12.89	537	22.25
12	1317	9.07	1024	11.67	512	23.34
13	1333	8.96	1106	10.80	586	20.39
14	1350	8.85	1236	9.67	622	19.21
15	1333	8.96	1268	9.42	707	16.90
17	1626	7.35	1430	8.36	825	14.48
18	1675	7.13	1595	7.49	927	12.89
19	1837	6.50	1756	6.80	1061	11.26

$$\frac{\beta_a \beta_c}{2.303 (\beta_a + \beta_c)} \quad (2.24)$$

The complex impedance spectra obtained in the cases of the specimens under test and control conditions led us to assume this reasonable value. This was because it was thought that assuming a reasonable value would be better than obtaining values of β_a and β_c through use of one anodic and one cathodic process. It was believed that the reaction rate control mechanism must have changed with the passage of time. Thus, use of values of β_a and β_c obtained during any particular period could not be justified. Reasonable values of β_a and β_c could have been obtained by the use of an anodic and a cathodic process in the case of the specimen in tap water. But to maintain uniformity, the value of 0.026 V was used in this case also. The corrosion rates obtained by using the above mentioned value seemed to be in quite good agreement with the corrosion rates obtained from the mass loss tests.

Figure 4.34 shows a comparison of the corrosion rates of the specimens in the three cases. As expected, the lowest corrosion rates were seen for the specimen under control conditions. Higher corrosion rates were seen for the specimen under test conditions. The highest corrosion rates were seen for the specimen exposed to tap water. These results further corroborated the theories proposed regarding the formation of scale layers with differences in porosity and thickness caused by RF treatment. Figures 4.35 and 4.36 show

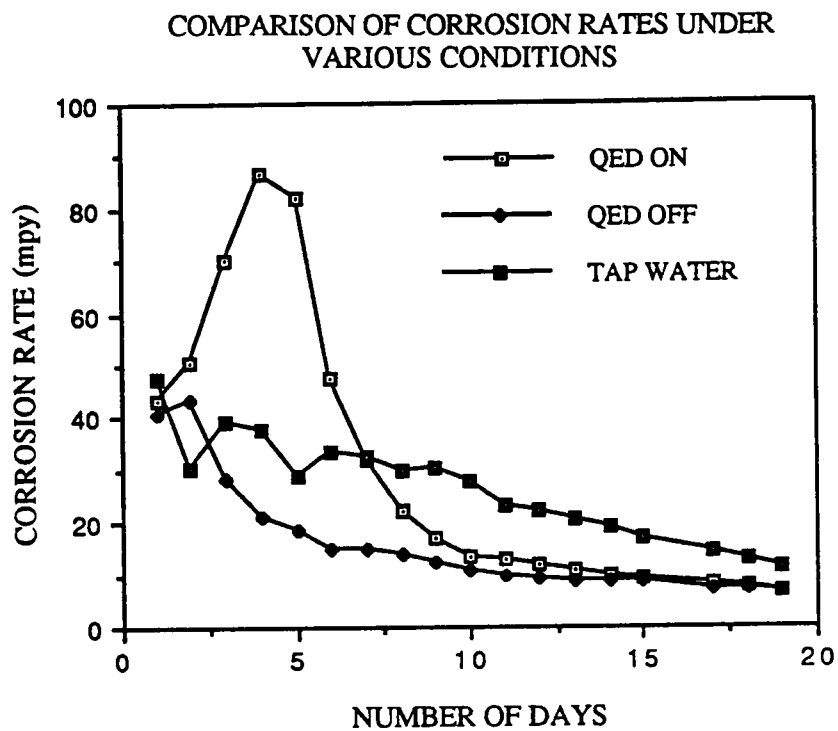


Figure 4.34 Comparison of corrosion rates of specimens exposed to various conditions.

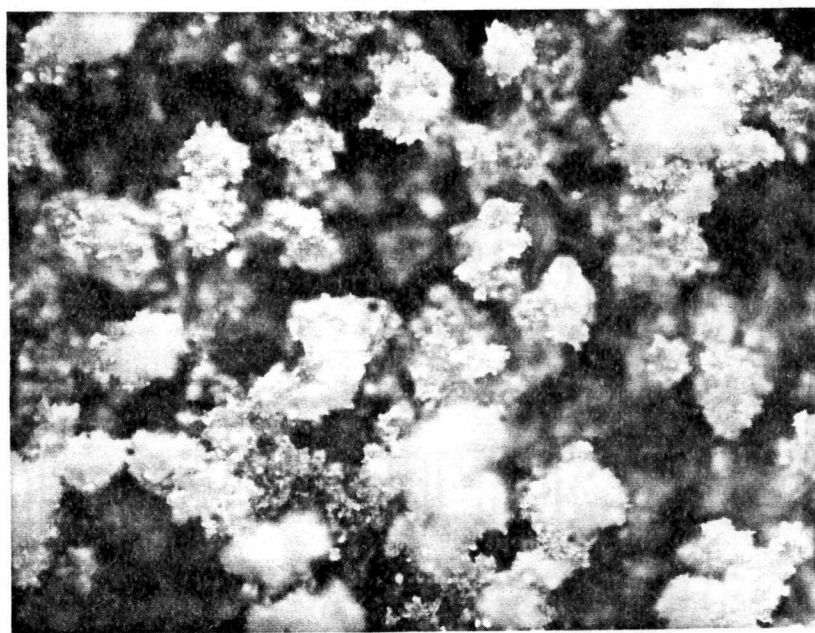


Figure 4.35 Photomicrograph of specimen after immersion in test medium under control conditions (Magnification: 100X).

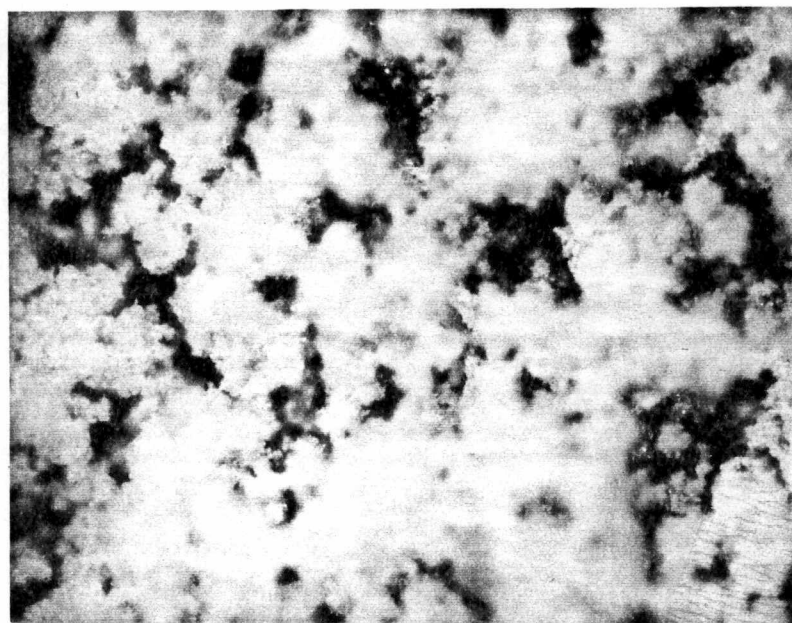


Figure 4.36 Photomicrograph of specimen after immersion in test medium under test conditions (Magnification: 100X).

photomicrographs of the specimens taken after exposures to the test medium under control and test conditions, respectively. The fact that the porosity of the scale layers formed was different can be seen in the photomicrographs. Thus, it is clear that the scale layer formed on the test specimen under test conditions was much more porous than the scale layer formed on the specimen under control conditions.

The fact that there was not much difference after 19 days in the corrosion rates of the specimens in the test medium under control and test conditions does not in any way refute the argument that the RF treatment slowed down scale formation. The corrosion rate of the specimen decreased even without any scale layer because of the presence of a corrosion product layer. This is seen in the case of the specimen exposed to tap water. The formation of a porous scale layer helped to further reduce an already decreasing corrosion rate.

Figures 4.37 through 4.42 show complex plane plots obtained in the case of a specimen in tap water with inhibitor. In one case, the inhibitor used was sodium nitrite (0.5 wt% per liter). In the second case, the inhibitor used was potassium dichromate (1 wt% per liter). Similar results were obtained in both the cases as can be seen in the complex plane plots. The plots for these two cases show straight lines. These results indicated a compact, non-porous passive layer on the surfaces of the specimens. Similar results were obtained by others while studying the impedance spectra of specimens in solutions containing inhibitors[25, 26]. The results obtained can be

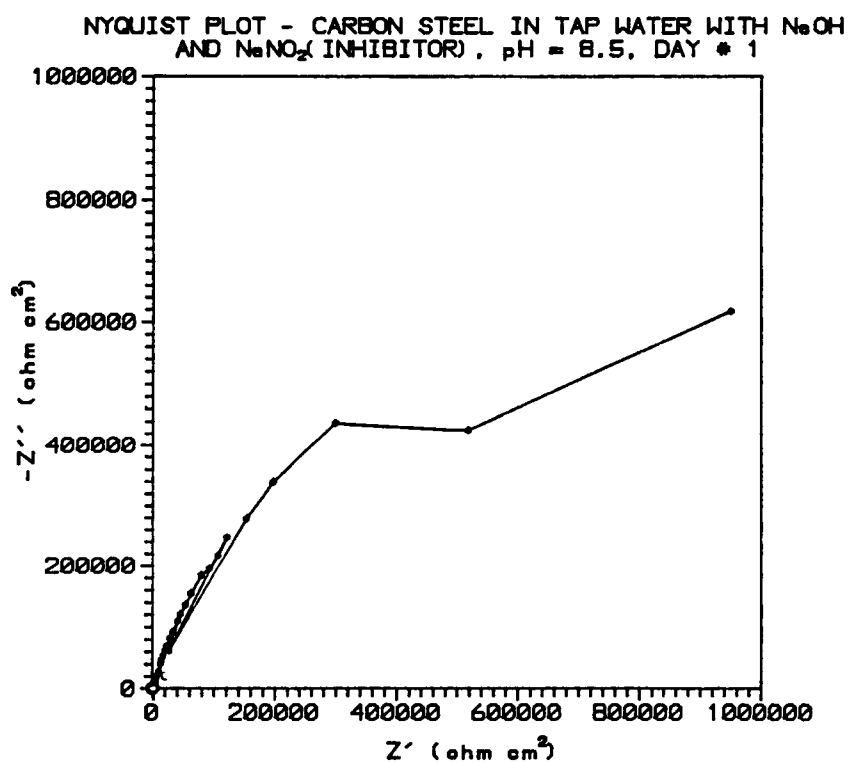
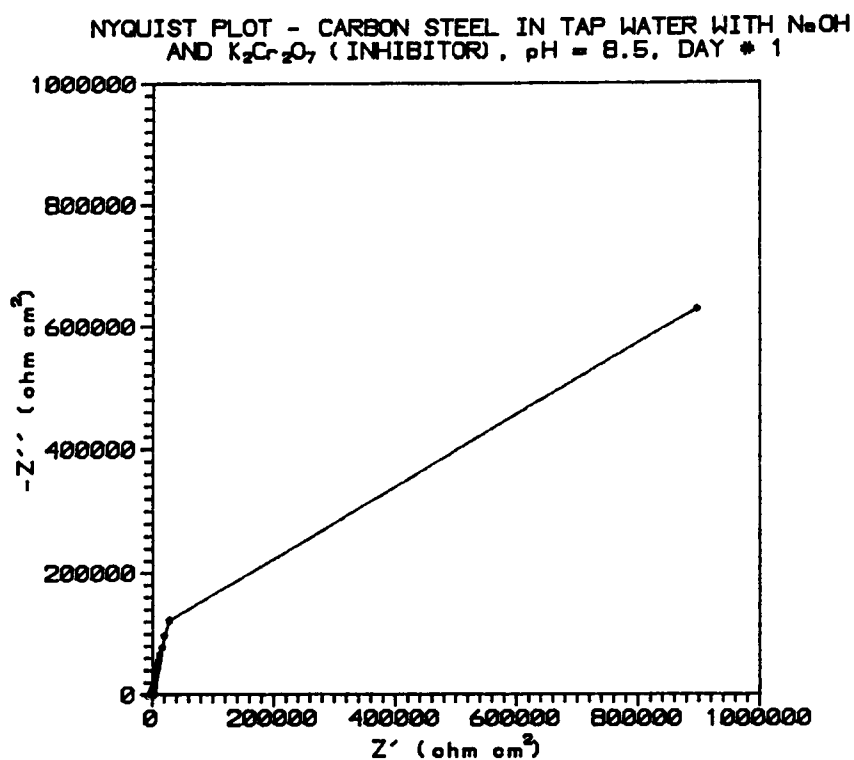


Figure 4.37 Complex plane plots for specimens in tap water with inhibitor after day 1.

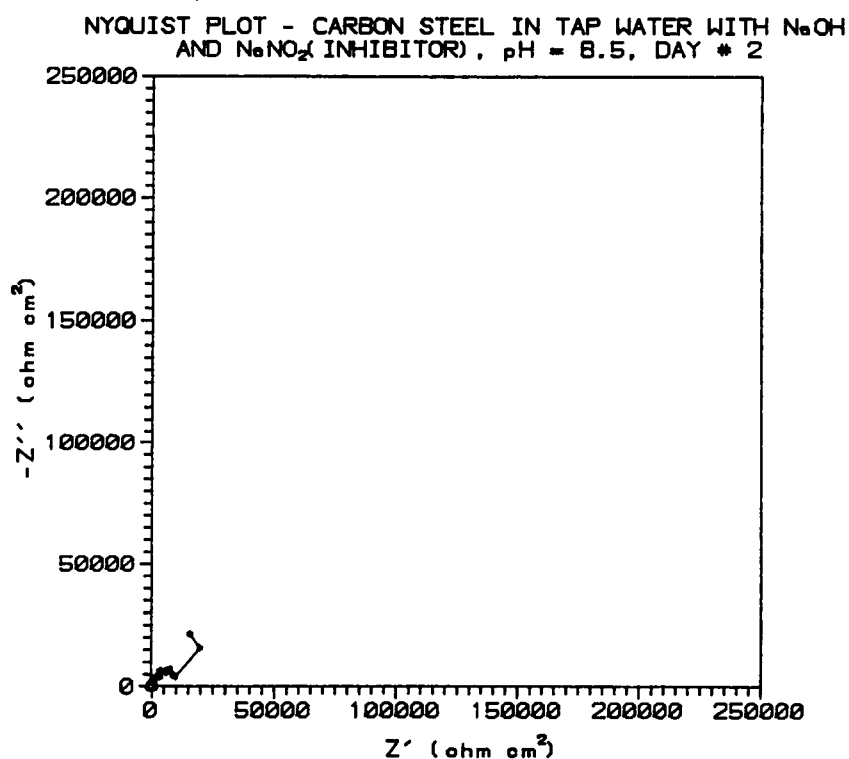
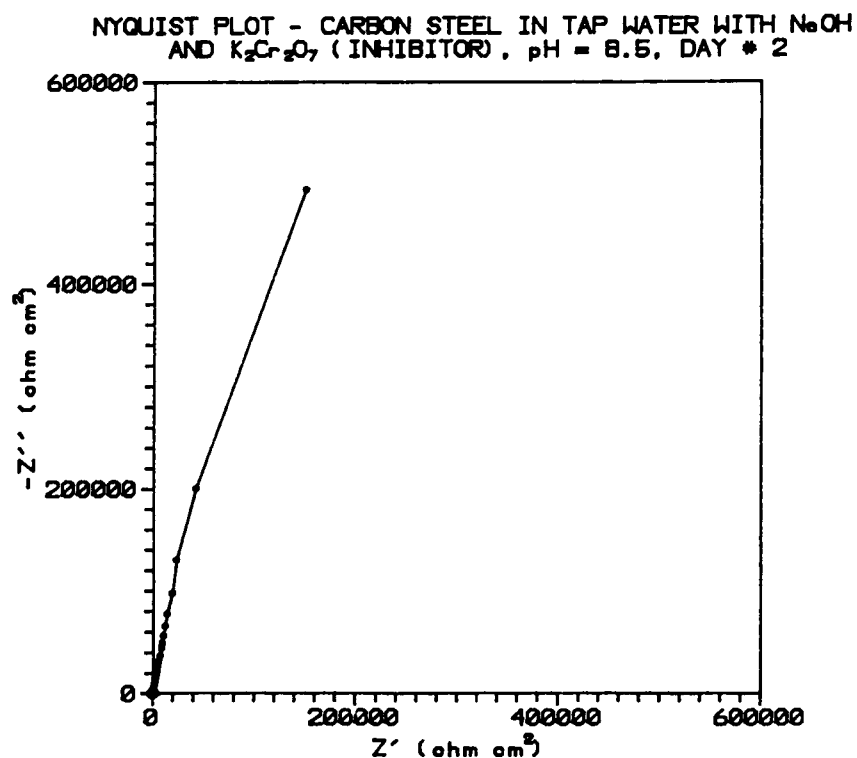


Figure 4.38 Complex plane plots for specimens in tap water with inhibitor after day 2.

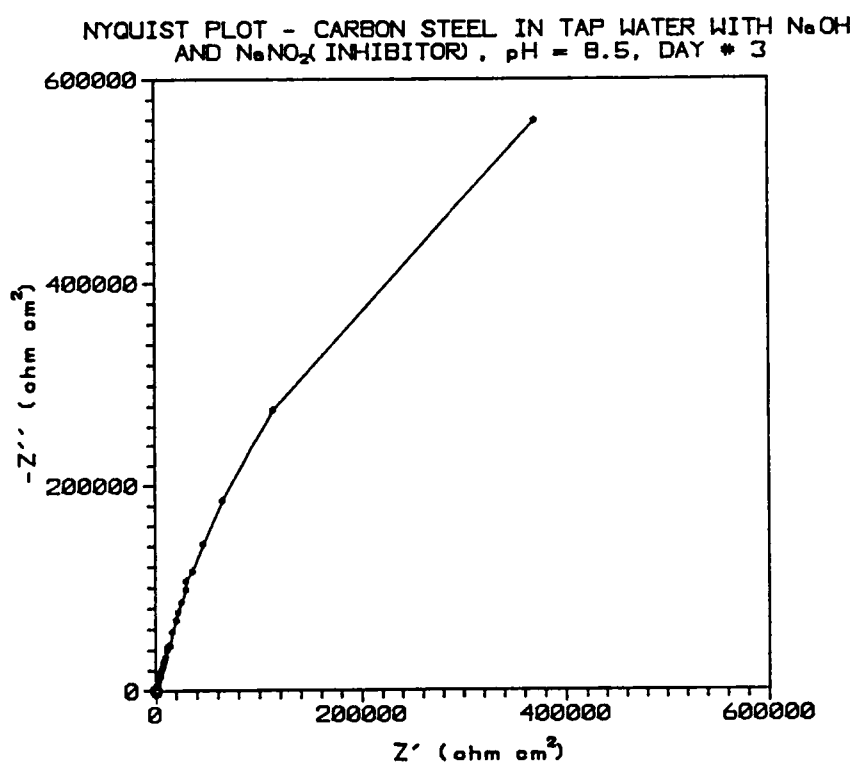
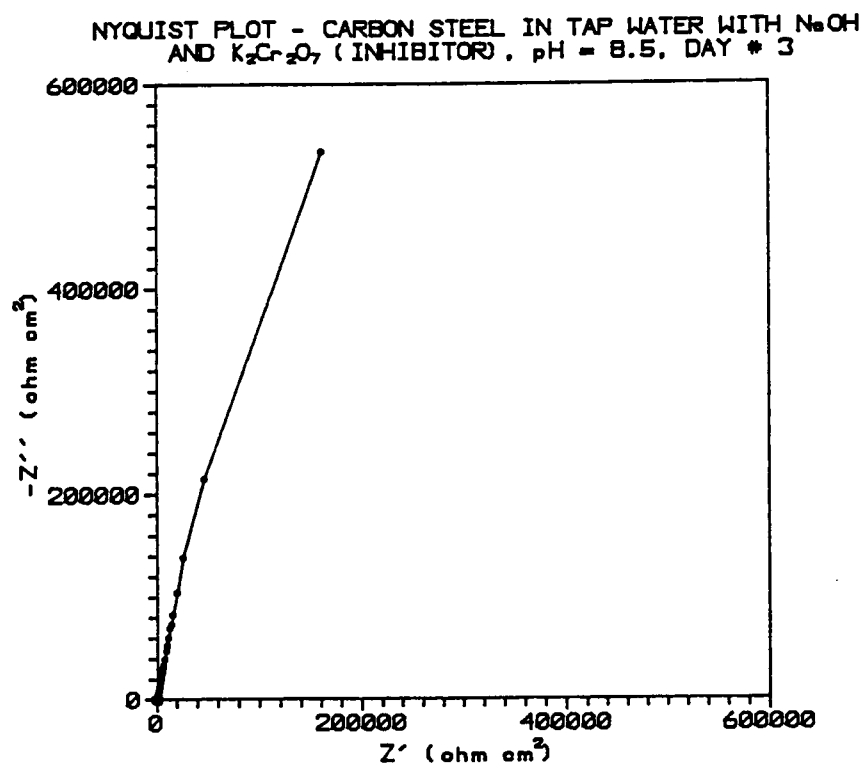


Figure 4.39 Complex plane plots for specimens in tap water with inhibitor after day 3.

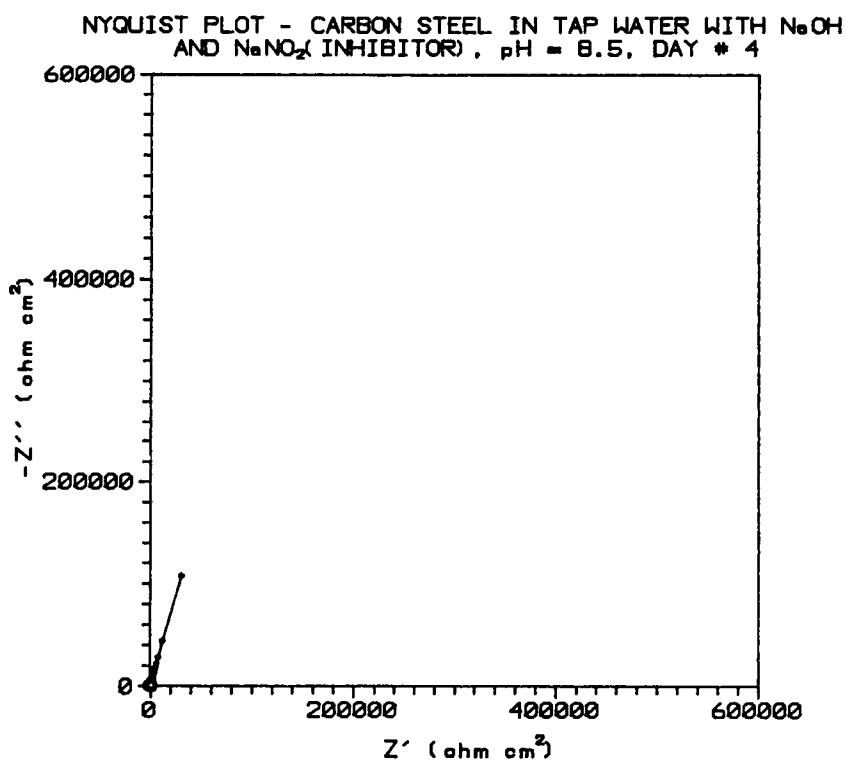
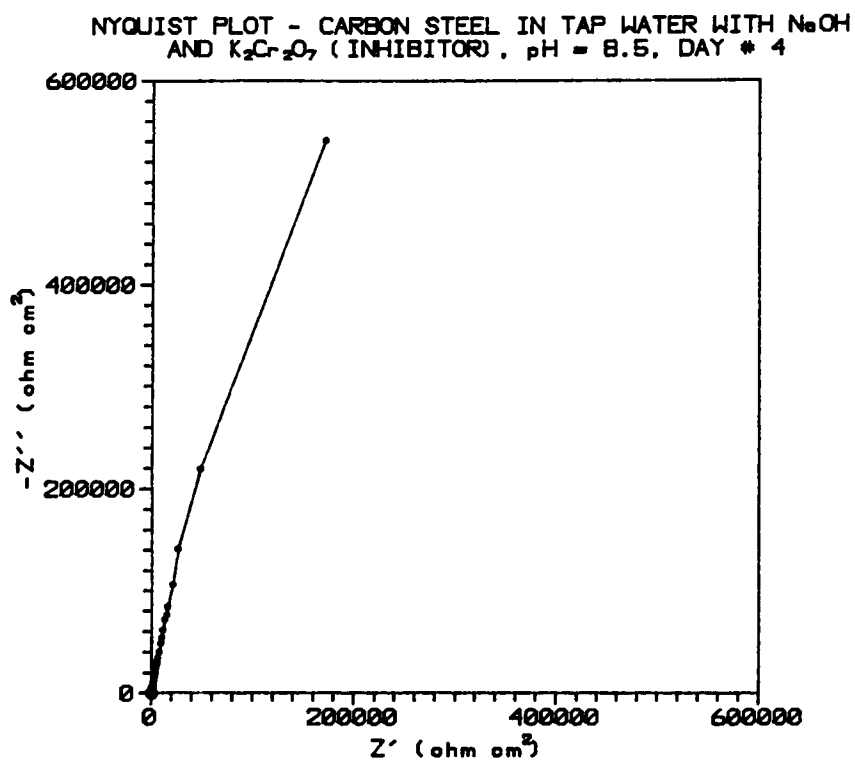


Figure 4.40 Complex plane plots for specimens in tap water with inhibitor after day 4.

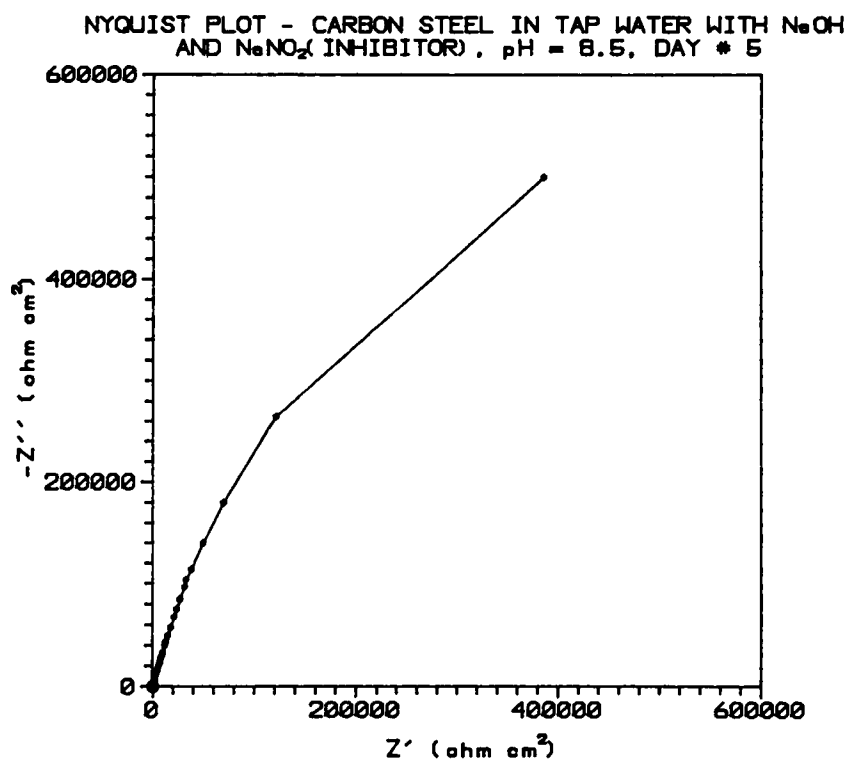
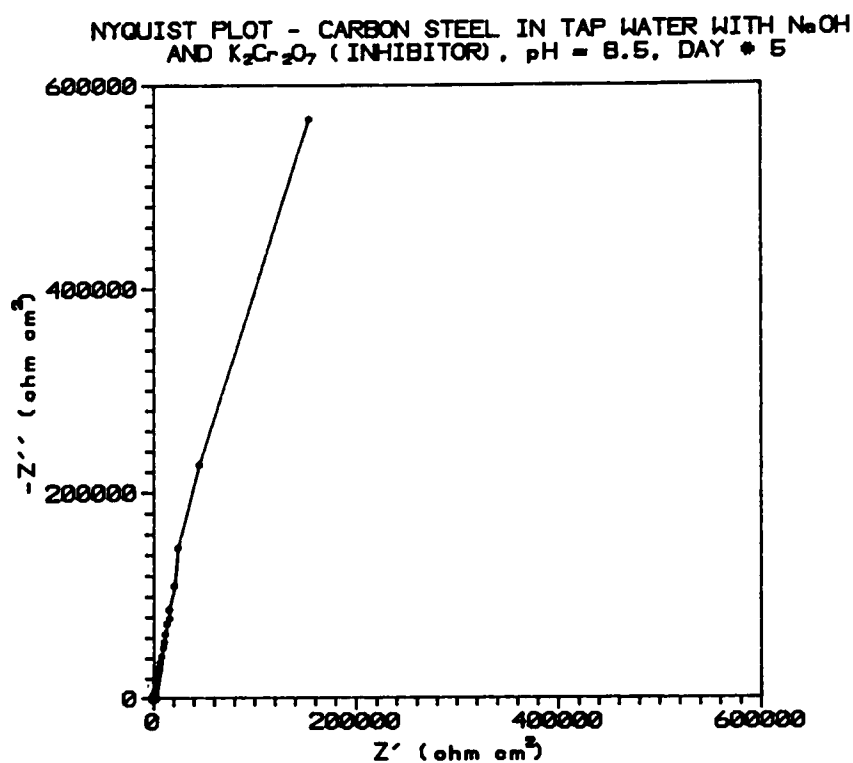
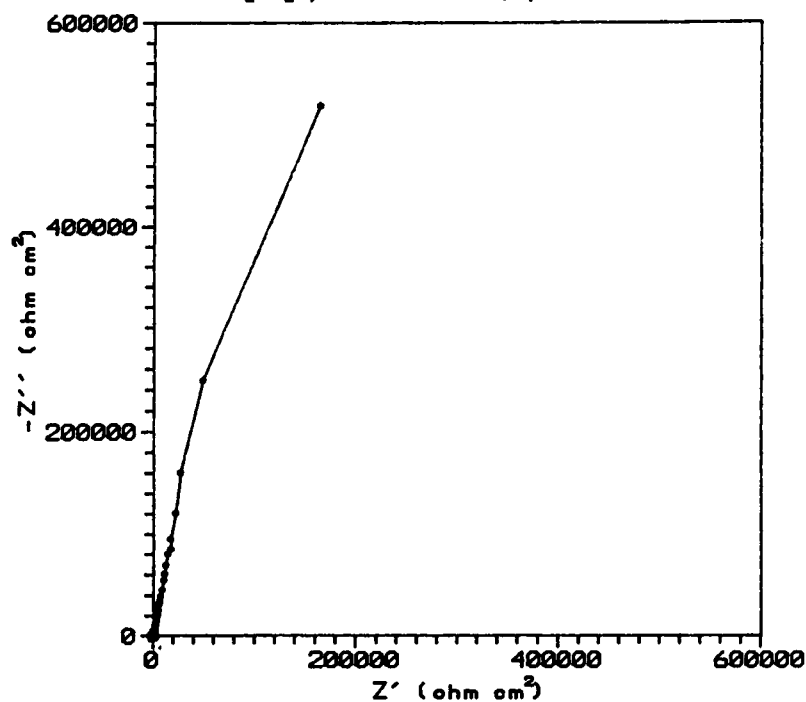


Figure 4.41 Complex plane plots for specimens in tap water with inhibitor after day 5.

NYQUIST PLOT - CARBON STEEL IN TAP WATER WITH NaOH
AND $K_2Cr_2O_7$ (INHIBITOR), pH = 8.5, DAY # 6



NYQUIST PLOT - CARBON STEEL IN TAP WATER WITH NaOH
AND $NaNO_2$ (INHIBITOR), pH = 8.5, DAY # 6

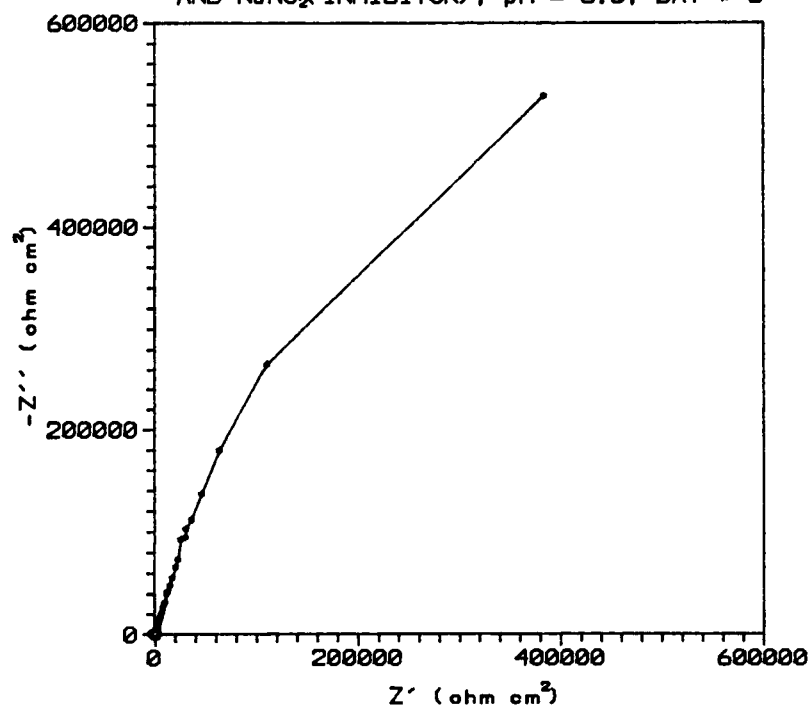


Figure 4.42 Complex plane plots for specimens in tap water with inhibitor after day 6.

modeled using the circuit shown in Figure 4.23. The results represent the special case when R_{po} tends to infinity. This would be the case if the specimens were left in the test medium under control conditions for a long time.

In general, it was assumed that in all cases the system was stable with respect to the chemistry of the test medium throughout the period of exposure. From the test data and the mechanisms proposed, it is clear that the RF treatment does slow down scale formation in water supersaturated with scale forming salts. It is also clear that the scale formed from the RF treated water is more porous than the scale formed from untreated water.

CHAPTER V

SUMMARY AND CONCLUSIONS

In order to study the effects of radio-frequency (RF) treatment of water on scale formation and corrosion, low-carbon steel specimens were exposed to continuously-circulating water supersaturated with calcium carbonate. RF treatments were performed with a quantum electrodynamic device (QED) manufactured by the Aqua Dynamics Group Corporation, Adamsville, Tennessee. The QED operated in the frequency range of 42.8 to 43.1 MHz with a peak-to-peak voltage range of 22 to 24 V. Exposures of the specimens in the supersaturated calcium carbonate solution (test medium) were conducted for 19 days either with the QED activated (RF treated test medium) or not activated (untreated test medium). Exposures were also conducted in tap water for 19 days without addition of calcium carbonate and without RF treatment (untreated tap water). The specimens were analyzed for corrosion by mass-loss measurements, microscopic surface examinations, and electrochemical impedance spectroscopy (EIS) measurements. The specimens were analyzed for scale formation by EIS measurements and microscopic surface examinations. The results of this study on the effects of RF treatment of water on scale formation and corrosion are summarized below.

The mass-loss measurements showed that the carbon steel exposed to the untreated test medium exhibited a lower corrosion rate (6.40 mpy) than when exposed to the RF treated test medium

(10.35 mpy). The highest corrosion rate was exhibited in untreated tap water (23.72 mpy). Surface examinations of the specimens, after removal of scale and corrosion products, showed that the roughening due to corrosion was lowest in the untreated test medium, higher in the RF treated test medium, and highest in the untreated tap water. These results were consistent with the mass-loss corrosion-rate measurements. The corrosion rates obtained from the EIS measurements showed the same relative trends as those obtained from the mass-loss measurements. The overall corrosion-rate results indicated that the RF treatment did not have a direct effect on the basic corrosion mechanism. Rather, the RF treatment modified the scale-formation mechanism, which in turn, had an indirect effect on the corrosion rate.

The EIS measurements indicated the presence of two layers on the surfaces of the specimens exposed to both the untreated and RF treated test media: a corrosion product layer adjacent to the metal surface and a scale layer on top of the corrosion product layer. The scale layer in the RF treated test medium was indicated to be thinner and more porous than in the untreated test medium. Furthermore, a time lag was exhibited in the RF treated test medium with respect to scale formation. Surface examinations immediately after exposures further corroborated the above results. Differences between the porosities of the scale layers formed in the RF treated and untreated test media were clearly evident.

In summary, the RF treatment of scale-forming water, as conducted in this investigation, slowed down the rate of scale formation on carbon steel. Further, the scale formed in RF treated water was more porous and thinner than the scale formed in untreated water. The corrosion rate, however, increased somewhat in the RF treated water. This result was attributed to a more porous, thinner scale which conferred less corrosion protection.

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