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ASPECTS OF THE ELECTROCHEMICAL BEHAVIOUR OF
IRON AND MILD STEEL

by Robert Donald Boalch

'A thesis submitted to Loughborough University
of Technology in fulfilment of the requirements
for the degree of Master of Philosophy'.

September 1983

Supervisor: Professor N.A. Hampson,
Department of Chemistry.

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The work described in this thesis has not been submitted, in full or in part, to this or any other institution for a higher degree.
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SUMMARY

The corrosion of ferrous materials is briefly reviewed. The theory and practice of the impedance methods currently used in the investigation of electrochemical corrosion reactions are described in some detail. Special reference is made to the differential capacitance bridge technique.

Using these methods the corrosion of both iron and mild steel in 1M sodium perchlorate under neutral pH conditions has been investigated. The effect of ions encountered in natural waters has also been explored, by addition to the base electrolyte. The work then examines the influence of a simple ortho-phosphate compound as an inhibitor of the corrosion reactions.

Confirmatory evidence is given to support the view that the point of zero charge on iron and mild steel is not attainable at neutral pH. The effect of alloying materials in mild steel is discussed.

The results of investigations with ortho-phosphate in the base electrolyte, containing added natural water constituents, are consistent with the repair of a protective film at the electrode.
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1. INTRODUCTION

All but a few metals find it thermodynamically favourable to revert to their oxides, from which they are often extracted. Thus, deterioration of a metal in contact with the atmosphere is a natural process.

Metallic corrosion is industrially important, for, as well as ensuring continuing sales for car manufacturers, it is potentially very expensive in terms of maintenance and replacement. The annual cost of corrosion in the United Kingdom is estimated to be well in excess of £1,000 million, so prevention is economically worthwhile.

Industrial installations are often constructed from mild steel which is relatively cheap and has satisfactory mechanical properties. It is, however, particularly susceptible to corrosion. The rate of corrosion will relate to the aggressiveness of the environment, and to cope with a wide range of practical situations there are a number of corrosion protection measures available (ranging from surface coatings to anodic and cathodic protection). Heat exchange units, fabricated from mild steel, are widely used in manufacturing industry and have their own unique corrosion problems.

The successful long term operation of these units requires clean heat exchange surfaces and low corrosion rates. These factors are, in untreated systems, mutually exclusive since deposition of material, chiefly calcium carbonate, retards corrosion by blocking diffusion of oxygen to the surface, but this barrier film has very poor heat transfer properties. Conversely, soft waters which deposit little calcium carbonate scale tend to enhance corrosion of the tubes.

Considerable work has been carried out to obtain chemical formulations which, when added to the circulating cooling water, are
able to minimise both scale formation and corrosion rate.

In order to investigate the processes of corrosion inhibition it is necessary to look first at the corrosion process itself.

The corrosion of iron has been widely studied, but largely in acid chloride or acid sulphate electrolytes. This work has been invaluable in establishing mechanisms for iron dissolution in acid media, but sadly there appears to have been very little progress made in the more technologically relevant areas such as the corrosion of mild steel in natural waters. Corrosion inhibitors have been fairly well studied by a variety of techniques, with some understanding of their general mode of action well established.

This present work reviews briefly the accepted mechanisms of iron dissolution and the effects of alloying impurities, and also reviews the various types of corrosion inhibitors in common use, and the mechanisms by which they work. Experimental results are presented from electrochemical studies (potentiostatic voltage-current data and faradaic impedance data) of the corrosion of iron and mild steel in 1M sodium perchlorate base electrolyte, with the addition of certain natural water constituents and an inorganic inhibitor compound.
2. THEORETICAL PRINCIPLES

The Electric Double Layer

In any study of electrode processes, it is important to have a knowledge of the region in which reactions occur i.e. the electrode-electrolyte interphase.

When a metal is immersed in an electrolyte solution, ions are lost from the metal into the solution, due to the difference in the potentials of each phase. Such a loss of ions gives rise to a nett negative charge at the surface, which tends to attract ions back to the metal. Thus, an equilibrium is set up where ions are leaving the metal, going into solution, and returning to the metal. At equilibrium the potential of the phases are equal and the flow of charge (current) in each direction is equal. This current is the exchange current, \( i_0 \), of the process. The exchange current is a measure of the rate at which the equilibrium potential is reached. The dynamic equilibrium which exists can be viewed as a static situation of charge separation.

This concept was the basis for models of the ionic distribution at the interphase.

The earliest model proposed for the structure of the interphase was due to Helmholtz\(^1\), who postulated the separation of positive and negative ions on either side of the solid-liquid boundary. This is analogous to a parallel plate capacitor, and gave rise to the term "electrical double layer". The model predicts capacitive behaviour of the interphase but does not allow for a resistive component, necessary if charge is to move across the interphase. Thus a change in electrode potential does not cause charge transfer but a change in
charge either side of the interphase.

Gouy\textsuperscript{2} and Chapman\textsuperscript{3} modified the Helmholtz model to take into account the thermal distribution of ions in solution, which resulted in the concept of a diffuse layer in the electrolyte to replace the compact layer of Helmholtz. Values of differential double layer capacitance calculated from the Gouy-Chapman theory differ markedly from experimentally obtained values, except in the potential region corresponding to zero charge (the potential of zero charge, p.z.c.). This discrepancy was a result of assessing the ions to be point charges.

Stern\textsuperscript{4} developed the idea that ions have finite size and would thus have a "plane of closest approach" to the electrode surface. The result of this is a model having a dense inner layer (Helmholtz layer) between the electrode and the plane of closest approach, then a diffuse layer from the plane of closest approach into the bulk solution. The potential difference between the metal electrode and solution is considered due to the potential difference of the dense inner layer and the diffuse layer. Following from these ideas the differential capacitance of the double layer can be attributed to the dense and diffuse regions in the following way:

\[
\frac{1}{C_L} = \frac{1}{C_1} + \frac{1}{C_2} \tag{I}
\]

where \(C_L\) is the differential double layer capacitance, \(C_1\) the differential capacitance of the dense layer and \(C_2\) the differential capacitance of the diffuse layer. This result shows the double layer being represented by two capacitors in series. Values of capacitance calculated from the Stern model show improved agreement with experimental results over the Gouy-Chapman model, in non adsorbing electrolytes. Graham\textsuperscript{5} took
into account adsorption of ions by further dividing the dense layer into two regions. First, a plane of closest approach of adsorbed ions, called the "inner Helmholtz plane" and second, a plane of closest approach for hydrated ions, termed the "outer Helmholtz plane". This is the widely accepted view of the electrical double layer, and it is shown schematically in Fig. 2.1.

The differential capacitance varies with potential, but experimentally it is found that if the change in potential is small (a few millivolts) the capacitance is unchanged. Hence the differential capacitance can be measured with an a.c. bridge using small voltage amplitude.

**IMPEDEANCE**

The models of the electrical double layer have accounted for the capacitance of the electrode in the absence of faradaic (charge transfer) processes. For charge transfer to occur it is necessary to have a current flowing across the double layer. This is envisaged as a resistance which is parallel to the double layer capacitance. This circuit will have an impedance to an applied a.c. signal and this forms the basis of a.c. impedance techniques. The electrochemical cell is considered as a combination of resistive, capacitive and inductive circuit elements each of which has a particular resistance to an a.c. signal (reactance). The expressions most commonly used for reactance are:

\[
\begin{align*}
\text{Resistive reactance, } X_R &= R \\ 
\text{Capacitive reactance, } X_C &= \frac{1}{j\omega C} \\ 
\text{Inductive reactance, } X_L &= j\omega L
\end{align*}
\]
Fig. 2.1 Gramme Model of the Double Layer
where \( j \) is \( \sqrt{-1} \), \( \omega \) is angular frequency \((2\pi f, f \) being the frequency of the applied waveform), \( R \) is resistance, \( C \) is capacitance and \( L \) is inductance.

A reactance or combination of reactances (impedance) can be defined by specifying its magnitude and phase angle (the angle its vector makes with the real axis), or by specifying the magnitude of the real (resistive) and imaginary (capacitive/inductive) components of the impedance.

Interpretation of impedance data has been based on the equivalent circuit, used by Randles\(^6\) in 1947, shown in Fig. 2.2. The total impedance of this circuit is:

\[
Z = R_{SO} + \frac{1}{j\omega C_L + \frac{1}{R_t + \frac{1}{1-j\omega}}}
\]

where \( C_L \) is the double layer capacitance, \( R_{SO} \) is the resistance of the electrolyte, and includes the resistance of the leads to the electrodes, \( R_t \) is the resistance necessary for faradaic processes to occur and \( \sigma \) the Warburg coefficient. The charge transfer resistance, \( R_t \), is related to the standard rate constant of the reaction \( k^\circ \), at equilibrium, by the equation

\[
R_t = \frac{RT}{n^2F^2C} \cdot \frac{1}{k^\circ}
\]

where \( R \) is the universal gas constant, \( T \) is absolute temperature, \( n \) is number of electrons transferred per reacting molecule, \( F \) is Faraday's constant, \( C \) is concentration of reacting species (at equilibrium \( C_{oxidised} = C_{reduced} \)). This situation, where charge transfer is wholly rate determining, rarely exists and complications due to diffusion need to be accounted for.
FIG. 2.2
Randles equivalent circuit

\[ R_d + C_d = W \]

FIG. 2.3. Randles plot of impedance data

\[ R \]
\[ R_t \]
\[ \frac{R}{\omega C} \text{ (ohms)} \]
\[ \frac{1}{\omega C} \]
\[ \omega^{-\frac{1}{2}} (s^{-\frac{1}{2}}) \]
Warburg calculated the concentration distribution of ions in the region of the electrode surface when applying a sinusoidal alternating current. Starting from Fick's second law of diffusion, Warburg derived expressions showing a "concentration wave" moving from the electrode into the bulk solution, and being one eighth of a cycle (45°) out of phase with the current. This change in concentration leads to a "diffusion overvoltage" which fluctuates sinusoidally. The relationship between the alternating current and the diffusion overvoltage is analogous to an equivalent resistive-capacitive circuit, whose impedance is the Warburg impedance, W. The expression derived for the Warburg impedance may be given as:

\[ W = \sigma \omega^{-\frac{1}{2}} - j\omega^{-\frac{1}{2}} \quad (VII) \]

and

\[ \sigma = \frac{RT}{n^2F^2C/D} \quad (VIII) \]

for a first order process, where \( \sigma \) is the warburg coefficient. Here D is the diffusion coefficient of the reacting species. There are two principal methods of presenting impedance data, for extraction of the reaction kinetics. The first is due to Randles who studied reactions of mercury amalgams, using an a.c. bridge (see Chapter 5). Randles obtained the Faradaic impedance of the cell as values of resistance and capacitance at a number of different frequencies. After elimination of solution resistance and double layer capacitance, leaving the faradaic impedance, Randles plotted each reactance against \( \omega^{-\frac{1}{2}} \), which yielded two parallel straight lines (Fig. 2.3). The capacitive component is through the origin, while the resistive component has an intercept equal to the charge transfer resistance, \( R_t \). The slope of the lines give the Warburg coefficient for the reaction, which is related to the concentration and the diffusion coefficient of the reacting species.
This ideal behaviour exhibited for charge transfer and diffusion controlled reactions has been developed further to account for deviations in the expected linear relationship between reactances \( R \) and \( \frac{1}{\omega C} \) and \( \omega^{-\frac{1}{2}} \). The deviation is considered due to chemical reactions, e.g. crystallisation or adsorption accompanying the charge transfer and diffusion processes. Anomalous behaviour due to chemical processes at the electrode is usually accounted for by placing additional components in the Randles circuit and determining their effect on the cell impedance. A full discussion of this procedure is given by Vetter\(^8\).

The second, and more modern, procedure for displaying impedance data is due to Sluyters\(^9\). Using the same equivalent circuit as Randles, Sluyters measured the total cell impedance over a range of frequencies. After separation of the real and imaginary components of the equivalent circuit, the following is obtained:

\[
Z = \left[ R_{SO} + \frac{Rt + \sigma \omega^{-\frac{1}{2}}}{(C_L \sigma \omega^{-\frac{1}{2}} + 1)^2 + \omega^2 C_L^2 (Rt + \sigma \omega^{-\frac{1}{2}})^2} \right] - j \left[ \frac{\omega C_L (Rt + \sigma \omega^{-\frac{1}{2}})^2 + \sigma \omega^{-\frac{1}{2}} (\omega \frac{1}{2} C_L^2 + 1)}{(C_L \sigma \omega^{-\frac{1}{2}} + 1)^2 + \omega^2 C_L^2 (Rt + \sigma \omega^{-\frac{1}{2}})^2} \right] \quad (IX)
\]

The imaginary, capacitive, reactance value is plotted against the real, resistive, reactance value for a range of frequencies. The shape of this type of plot has been predicted mathematically for high and low frequencies where distinctive behaviour is observed. At high frequency, and with an irreversible reaction, the effects of the Warburg impedance, \( \sigma \omega^{-\frac{1}{2}} \), will be small (as \( \omega^{-\frac{1}{2}} \to 0 \)) with respect to the charge transfer resistance \( Rt \). After rearrangement of the expressions for the resistive and capacitive components of impedance, ignoring the Warburg terms, and eliminating \( \omega \), an expression relating the real and imaginary terms was obtained:

\[
\left| ReZ - R_{SO} - \frac{Rt}{2} \right|^2 + \left| ImZ \right|^2 = \left| \frac{R_t}{2} \right|^2 \quad (\alpha)
\]
where ReZ and ImZ are the real and imaginary components of impedance respectively. Thus a plot of ReZ against ImZ at high frequencies forms a circle with its centre on the real axis (Fig. 2.4). The circle intersects the real axis at Rs0 at infinite frequency, and at Rs0 + Rt at zero frequency. At low frequency and with a reversible reaction, distortion of the circle occurs due to the increasing contribution of diffusion. At low frequencies the Warburg terms \( \omega^{-1} \) are important. By keeping terms containing \( \omega^{-1} \) but neglecting higher order terms of \( \omega \) the ReZ and ImZ equations are formed from the overall impedance equation. Then by eliminating \( \omega \) completely the relationship between ImZ and ReZ is obtained:

\[
\text{ImZ} = \text{ReZ} - Rs0 - Rt + 2a^2C_L \tag{XI}
\]

This indicates a plot of ImZ against ReZ and will be a straight line of slope 1 (Fig. 2.5), which intersects the ReZ axis at infinite frequency, at \( Rs0 + Rt - 2a^2C_L \).

By using the 'complex plane' method of Sluyters it is possible to obtain the charge transfer resistance for the reaction from impedance data. The kinetic information i.e. exchange current density and rate constant may be obtained by the same procedure used by Randles.

The complex plane plot for experimental impedance data rarely shows all charge transfer control or all diffusion control and typical behaviour is shown in Fig. 2.6. Here the high frequency semi-circle is followed by deviation towards a straight line, ideally at 45\(^\circ\) to the real axis. The charge transfer resistance may be found from the diameter of the semi-circle, as already discussed.

As with Randles plots the complex plane plot will show variation from this ideal behaviour if any extra processes are occurring at the
Fig. 2.4 Complex plane display – charge transfer control

Fig. 2.5 Complex plane display – diffusion control
Fig. 2.6  Complex plane display - mixed control
electrode, which are not accounted for in the Randles equivalent circuit. Flattening of the semi-circle is a common effect and has been considered due to surface inhomogeneities\(^\text{10}\). The appearance of a second semi-circle has been attributed to adsorption effects\(^\text{11}\). A considerable amount of work has been carried out on the effect of different types of reaction on the complex plane display by Armstrong and co-workers\(^\text{12,13,14}\), and Epelboin and co-workers\(^\text{15,16}\).

Faradaic impedance data, obtained as series circuit components, may be transformed to give the equivalent parallel circuit arrangement (Fig. 2.7). In order to do this an estimate of solution resistance \(R_{SE}\) was made from an extrapolation of the appropriate complex plane plot to infinite frequency, then subtracted from the measured series resistance. Using a transformation constant \(\beta\), \(\beta = \frac{1}{\omega C_{SE}(R_{SE}-R_{SO})}\) where \(C_{SE}\) is the measured series capacitance and \(R_{SE}\) the measured series resistance) the values of the equivalent parallel circuit components were calculated:

\[
C_p = \frac{\beta^2}{(1+\beta^2)} \quad C_{SE} \quad \text{(XII)}
\]

\[
R_p = (1+\beta^2) \quad R_{SE} \quad \text{(XIII)}
\]

After assuming the charge transfer resistance of the reaction under study is zero and the concentration of reduced species (the metal) is much greater than the concentration of oxidised species, denoted \(C_o \quad \text{(mol cm}^{-3}\), Giles et al\(^\text{17}\) derived the expressions

\[
C_p = C_L + \frac{C_o}{2\sigma \omega^2} \quad \text{(XIV)}
\]

and

\[
R_p = \frac{2\sigma}{\omega} \quad \text{(XV)}
\]
FIG. 2.7

Series to Parallel circuit transformation

\[ R_p = (1+\beta^2)(R_{se} - R_{so}) \]

\[ C_p = \left( \frac{\beta^2}{1+\beta^2} \right) C_{se} \]
This parallel circuit analysis has been extended further to account for an apparent parallel capacity due to surface roughness. This additional capacitance, proportional to $\omega^{-\frac{1}{2}}$, was incorporated into the parallel capacitance expression:

$$C_p = C_L + \frac{C_0}{2\omega^{\frac{1}{2}}} + \frac{g}{\omega^{\frac{1}{2}}}$$  \hspace{1cm} (VI)

where $g$ is the surface roughness factor.

Thus plots of $R_p$ and $C_p$ against $\omega^{-\frac{1}{2}}$ can yield the double layer capacitance, surface concentration of oxidised species (which requires the Warburg coefficient) and information on the degree of roughening of the surface during reaction.

Such plots for data obtained with an iron electrode are useful over a fairly limited range of potential due to the formation of surface films resulting in non-linearity$^{18}$.  

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3. THE DISSOLUTION OF IRON

A very large number of studies have been carried out to elucidate the mechanism and kinetics of iron dissolution, the majority of these in acid chloride and acid sulphate electrolytes.

Despite the many and varied studies into iron dissolution, there are some points common to the majority of them. These may be summarised as follows.

Dissolution takes place by a number of consecutive steps, one of which is rate determining, and steps other than the rate determining step (rds) are considered to be at equilibrium (allowing application of steady state kinetics to the system).

Hydroxyl ions play an important role in the reaction scheme, even in acidic solution, and the experimental determination of reaction order \(\frac{d \ln i}{d \ln C}\) with respect to hydrogen or hydroxyl ions has been common to many studies.

The experimental determination of Tafel slopes \(\frac{dE}{d \ln i}\) and of anodic transfer coefficients has been widely used to identify the rds of a proposed mechanism.

One of the first published studies which recognised the effect of pH (or more correctly pOH) on the dissolution of iron was due to Kabanov, Burstein and Frumkin\(^{19}\). Their mechanism can be summarised thus;

1. \(Fe + OH^- \rightarrow (FeOH)_{ads} + e^-
\)
2. \((FeOH)_{ads} + OH^- \rightarrow (FeO)_{ads} + H_2O + e^-
\)
3. \((FeO)_{ads} + OH^- \rightarrow (HFeO_2^-)_{sol} \)
The formation, in step one, of an adsorbed surface layer of FeOH is widely accepted as the first step in the mechanism of iron dissolution. The rds in this mechanism is step two. According to this scheme the anodic transfer coefficient and the reaction order with respect to OH\textsuperscript{−} are predicted as 1.5 and 2 respectively. These were confirmed experimentally.

An interesting observation made by Kabanov et al that dissolution in alkali proceeds much more rapidly than in acid at the same potential led them to conclude that the mechanisms of iron dissolution in alkali and acid were considerably different. Hurlen\textsuperscript{20} studied iron dissolution in alkaline solution and obtained results apparently at variance with Kabanov et al. However, he was able to show that his own results and those of Kabanov et al were in good agreement for anodic iron dissolution in alkaline solution, having an anodic transfer coefficient of 2 and being first order with respect to OH\textsuperscript{−}. Hurlen also strongly suggests that the results of Kabanov et al were due to the anodic hydrogen reaction on the active iron electrode (the anodic transfer coefficient and reaction order with respect to OH\textsuperscript{−} for this reaction were found to be 1.5 and 2 respectively).

Bonhoeffer and Heusler\textsuperscript{21} and Heusler\textsuperscript{22} investigated the dissolution of iron in acidic solutions and confirmed the importance of hydroxyl ions in the dissolution of iron. In an earlier paper\textsuperscript{23} Bonhoeffer and Heusler had explained the increased dissolution rate of iron in alkaline solution as being due to surface coverage of hydrogen, retarding the reaction in acid.

The mechanism of iron dissolution in acid, due to Heusler, may be summarised as:
1. \( \text{Fe} + \text{OH}^- \rightleftharpoons (\text{FeOH})_{\text{ads}} + e^- \)

2. \( (\text{FeOH})_{\text{ads}} + \text{Fe} \rightleftharpoons \text{Fe(FeOH)}_{\text{ads}} \)

3. \( \text{Fe(FeOH)}_{\text{ads}} + \text{OH}^- \rightarrow (\text{FeOH})_{\text{ads}} + \text{FeOH}^+ + 2e^- \)

4. \( \text{FeOH}^+ + \text{H}^+ \rightleftharpoons \text{Fe}^{2+} + \text{H}_2\text{O} \)

Step 3 is considered the rds.

In acid solution \( \text{OH}^- \) concentration is enhanced near the electrode surface. Heusler examined the dissolution reaction experimentally under both steady state and transient conditions and obtained transfer coefficient and reaction order, with respect to \( \text{OH}^- \), of 2 and 2, and 1 and 1 for each. The application of steady state kinetics to the proposed reaction scheme predicts a transfer coefficient of 2 and a reaction order of 2, as found by Heusler. Heusler also argued that his transient data fit his mechanism, despite the non-equilibrium of reactions 1 and 2, by assuming a constant concentration of \( \text{Fe(FeOH)} \). However, the major problem with this mechanism is the rate-determining step, which requires a two electron-transfer.

This problem was eliminated by Bockris and co-workers\(^{24,25}\) who, using both their own experimental data and relevant published data, formulated modified mechanisms of iron dissolution. The experimental results of Bockris, Drazic and Despic are consistent with the following mechanism, which they proposed:

1. \( \text{Fe} + \text{OH}^- \rightleftharpoons \text{FeOH} + e^- \)

2. \( \text{FeOH} \rightarrow \text{FeOH}^+ + e^- \)

3. \( \text{FeOH}^+ \rightleftharpoons \text{Fe}^{2+} + \text{OH}^- \)

Here reaction 2 is the rds. The experimental data which fit predictions for this mechanism are an anodic transfer coefficient of 1.5 and a
reaction order, with respect to OH\(^-\), of 1.

After recognising the importance of hydroxyl ions in the anodic dissolution of iron a number of studies took place examining the effects of competing anions, which generally reduce the dissolution rate\(^{25,26,27}\). This effect has largely been explained in terms of adsorption of the ions blocking the surface to OH\(^-\) ions. Halide ions are believed to accelerate the dissolution, but this effect is much weaker than that due to OH\(^-\). Sulphates may enhance dissolution but this is due, in part, to their tendency to increase pH.

It seems generally agreed that elucidation of reaction mechanisms on the basis of experimental data, as already described, have difficulties, particularly in interpretation of fractional reaction orders.

Hilbert et al\(^ {28}\) have proposed that iron dissolution may occur by one of two different mechanisms according to the state of its surface. A sample low in lattice defects and adsorbed matter (hot worked in a hydrogen atmosphere as used by Bockris et al\(^ {25}\)) dissolves according to the non-catalysed Bockris mechanism. In systems where the electrode has a high concentration of surface defects (e.g. after cold working) its dissolution will occur according to the catalysed Heusler mechanism. Hilbert et al have demonstrated the different mechanisms for cold worked (up to \(\sim 500^\circ\text{C}\)) and hot worked (above \(750^\circ\text{C}\)) samples, with intermediate states between these two. Bignold and Fleischmann\(^ {29}\) studied iron dissolution in acid using a transient technique and proposed that formation of hydroxide intermediates occurs at kink sites on the surface. The rds is then movement of these hydroxide species onto the surface.

Evidence has also been presented\(^ {30}\), and later discussed\(^ {31,32}\).
demonstrating two different anodic reactions which are potential
dependent. At low anodic potentials dissolution takes place according
to the mechanisms already discussed. A second, parallel reaction
predominates at higher anodic potentials which changes the kinetics
of the dissolution process.

A useful review of the mechanisms of iron dissolution in acid
solutions, covering the work before 1967, was published by Florianovich
et al\textsuperscript{33}. Ten years later Ammar\textsuperscript{34} presented a brief review of the
widely accepted mechanisms and the experimental data used in forming
them. He then showed, from steady-state kinetics, that other mechanisms
could be postulated which would agree with the most commonly obtained
experimental data.

There appears to be a shortage of published data concerning
electrochemical studies of the anodic dissolution of ferrous alloys.
However, much of the information given for iron dissolution can be
qualitatively applied to alloys. Stressed areas of metal tend to be
anodic relative to unstressed areas and hence dissolution is enhanced
at points of stress\textsuperscript{35}. Thus cold worked metals are likely to corrode
more readily than heat treated ones. Heat treatment also causes
changes in the state of combination of carbon and in grain size.
Increase in grain size (as occurs with heat treatment) in itself does
not increase susceptibility to corrosion. This has been reported for
the case of fusion welding, where the grain size around the weld is
larger than that away from the weld\textsuperscript{36}. The carbon within the iron
does not have a significant effect on the overall corrosion rate\textsuperscript{37}.
It was observed here though that iron carbide (Fe\textsubscript{3}C) was not attacked
to the same extent as ferrite (which is low in carbon). The iron
carbide is considered cathodic to other phases and this can enhance
pitting corrosion. Normal amounts of sulphur and phosphorous (up to
about 0.07\% and 0.1\% respectively) appear to have little effect on the
corrosion of mild steels. Manganese, in the form of manganese sulphide, increases damage by cracking, particularly between the manganese sulphide-ferrite areas\textsuperscript{38}.

The alloying of chromium and nickel with iron to produce stainless steels considerably change the physical and electrochemical properties of the material. Here, however, the main concern is the corrosion behaviour of mild steels.

Speller\textsuperscript{39} and Uhlig\textsuperscript{40} both deal with the corrosion of iron-carbon alloys in some detail.
4. CORROSION PREVENTION

The Pourbaix Diagram

A useful tool in predicting the state of a metal in an electrolyte solution is the potential-pH diagram. This type of diagram has been constructed for a wide variety of systems by Pourbaix, after whom they are named. These diagrams are essentially an isothermal phase diagram showing the calculated metal-ion-oxide equilibria with respect to potential and pH. The important feature of the diagram is its division into three regions:

1. immunity - where the activity of metal ions is less than $10^{-6}$ mol dm$^{-3}$.
2. corrosion - where the activity of metal ions, or complex ions, is greater than $10^{-6}$ mol dm$^{-3}$.
3. passivity - where the metal compounds formed are solid and provide a protective surface layer.

The main limitations of these diagrams are:

a) they yield no kinetic information
b) corrosion often takes place below the Pourbaix criteria
c) if hydroxide precipitation occurs away from the surface passivity is not achieved.
d) the production of OH$^-$ and H$^+$ may cause localised pH changes which are not detected by bulk measurement.

The region of water stability has also to be considered to avoid polarising the electrode into hydrogen or oxygen evolution, where the potential-pH diagram indicates immunity or passivity. The metal-water phase diagram can be significantly affected by anions, particularly chloride which forms soluble complexes and thus extends the zone of corrosion.
The potential-pH diagram for iron is shown in Figure 4.1. From the diagram it is seen that iron corrodes freely over a wide range of pH, but particularly in acid and very strong alkali. There is a small region of passivity between pH 8 and pH 14.

The discontinuous lines mark the conditions of water stability. Below the lower lines hydrogen evolution may occur and above the upper line oxygen evolution may occur. In practice this water stable region can be extended beyond these theoretical lines.

From the iron-water phase diagram three methods of corrosion protection are apparent.

**Cathodic Protection**

The potential of the metal forced into the zone of immunity engenders cathodic polarisation. If the potential of the metal is lowered to the reversible potential of the anodic reaction (typically \( M = M^{n+} + n e^- \)) then the overall loss of metal ions is compensated by the deposition of metal. This is shown schematically with a potential-current diagram for both cathodic and anodic reactions (Fig. 4.2).

At the mixed corrosion potential, \( E_{CORR} \), the rate of corrosion is \( i_{CORR} \). As the potential is reduced a current, denoted \( i_{ext} \), is required and the corrosion rate drops to \( i'_CORR \). When the potential is depressed to the reversible anode potential the structure is completely protected. \( i_{ext} \) is proportional to \( i_{CORR} \). In practice metal ions, \( M^{n+} \), in the environment are at very low concentrations and from the Nernst equation the potential required for complete protection will be lower than the standard reversible potential for the anode reaction.

Cathodic protection is never used in acid environments where \( i_{CORR} \) is large and hydrogen evolution is the cathodic reaction. The main uses
Fig. 4.1 Potential-pH equilibrium diagram for the system iron-water. (after Pourbaix et al.)
FIGURE 4.2: SCHEMATIC POTENTIAL - CURRENT DIAGRAM FOR THE ANODIC AND CATHODIC REACTIONS ON A CORRODING METAL IN AN ELECTROLYTE SOLUTION.
of cathodic protection are structures in a neutral environment with a continuous electrolyte (aqueous solutions and soils of low resistance).

The current for protecting the metal, \( i_{\text{ext}} \), can be supplied by natural galvanic corrosion or an impressed current.

The former requires a material with a substantially lower potential than the structure to be protected. By connecting a structure to the anodic material, this dissolves and supplies current for the protection of the structure. Such anodes, which dissolve and require regular replacement, are termed sacrificial anodes, and for ferrous metal protection are often magnesium or zinc. The second technique requires a d.c. supply which is connected to both the item to be protected and an inert anode (immersed in the same electrolyte). The structure is cathodically polarised by the d.c. supply. The anode is selected so that it does not dissolve but has a cathode reaction such as oxygen evolution (hence the term inert anode).

Cathodic protection is used in fresh water and marine environments and may be used for buried structures in certain soils. Protection of bare steel structures is expensive due to the high current requirement, so cathodic protection is most often used in conjunction with surface coatings. In such cases the current used is to protect bare metal where the coating has been broken.

**Anodic Protection**

This raises the potential of the metal to produce passivity. This technique may, in theory, be used for protecting any metal which exhibits a passive state. In practice, the item to be protected, usually a tank containing a corrosive, conducting liquid, is connected
to a potentiostat as the working electrode. A counter and reference electrode are immersed in the electrolyte within the vessel, and connected to a potentiostat.

In order to passivate the metal completely the vessel is anodically polarised so that the potential exceeds the Fladé potential\textsuperscript{43} (the potential of the active-passive transition), and in order to achieve this the current has to exceed the maximum corrosion current. However, after supplying a large current to induce passivity the current requirement falls very considerably. To maintain passivity the potential has to be held in the passive region. The small current flowing while the metal is passive, is a measure of the dissolution rate of both the film and the underlying metal so corrosion is not stopped, but is considerably reduced.

Anodic protection is often applied to mild steel vessels containing sulphuric, phosphoric and nitric acids and aqueous ammonia solutions, where despite high capital outlay it is still cheaper than stainless steel or lined vessels. The equipment for anodic protection is portable so it is widely used for mobile tankers. By careful selection of electrolyte some metals and alloys can be passivated without using an external power supply. The requirements for this are that the redox potential of the solution, and the mixed corrosion potential, must exceed the Fladé potential and the rate of the cathodic process has to be greater than the maximum rate of corrosion (high exchange current). To illustrate this mild steel in concentrated nitric acid is passivated. However, dilute nitric acid, having a lower potential, is unable to passivate mild steel and rapid corrosion occurs.
Induce passivity by changing pH

Increasing the pH of the environment can move iron into passivity. An example of this is adding sodium hydroxide to boiler feed water, which, in the presence of small amounts of oxygen, forms a passive layer of Fe$_3$O$_4$.

Corrosion inhibition of ferrous alloys in aqueous environments

Corrosion within vessels and pipework, containing aqueous solutions, can often be dramatically reduced by adding small amounts of chemicals to the liquid. The resulting drop in corrosion rate may not always be predicted by a Pourbaix diagram due to the low concentration of additive.

Inhibitor materials are chemically diverse and, historically, it seems that they have largely been discovered by trial and error (or accident!).

The classification of corrosion inhibitors is frequently by the electrochemical terms anodic or cathodic. The corrosion reaction consists of both anodic dissolution of metal and a corresponding cathode reaction (typically $O_2 + 2H_2O + 4e \rightarrow 4OH^-$ in neutral aqueous solution). A reduction in the rate of either the anodic or cathodic reaction will reduce the overall corrosion rate. The terms anodic and cathodic refer then to the reaction which they inhibit. A third group inhibit both reactions and may be termed mixed inhibitors. This classification has to be modified however to account for the state of the metal. In acid solutions where the metal surface is often free of oxide films
adsorption of the inhibitor is important, while in neutral or alkaline solutions inhibitors often serve to stabilise existing passive films\textsuperscript{45}.

The inhibitors may be loosely grouped together according to their chemistry but such grouping often fails with more complicated, modern formulations. The basic groups of inhibitors are listed below with a brief description of their proposed mode of action and practical applications.

\textbf{Metallic cations}

Some metallic cations inhibit corrosion. A relevant example is the inhibition of steel corrosion in acid solutions by the addition of tin ions (a tin ion concentration of 0.004M giving slightly more than a ten fold decrease in corrosion rate)\textsuperscript{46}. Tin ions have been used in acid cleaning solutions for boilers to minimise the corrosive effects of ferric ions (from Fe\textsubscript{2}O\textsubscript{3})\textsuperscript{47}. Arsenic\textsuperscript{46}, cadmium, manganese and zinc\textsuperscript{48} all show signs of inhibiting steel corrosion in acids, but their use is limited by their high toxicities. The use of metallic ions as inhibitors and their proposed mechanisms of inhibition have been reviewed by Leidheiser\textsuperscript{49}.

\textbf{Inhibitive Anions}

There are various inorganic anions which act as corrosion inhibitors for ferrous alloys, most of which are classed as anodic inhibitors, due to their preferential inhibition of anodic processes. It has been observed that some anions, notably chromate and nitrite, are able to inhibit corrosion in the absence of oxygen while for other e.g. phosphate, carbonate and silicate, oxygen is essential for successful inhibition\textsuperscript{50}. The operation of these inhibitors is
generally viewed in terms of chemical passivation\(^{51}\), which has already been discussed for mild steel in concentrated nitric acid. The success of the inhibitor will depend on the redox potential of the inhibitor, the cathodic Tafel slope and exchange current of the reduction process, and the Flade potential and maximum corrosion current of the metal.

Chromate and nitrite are fairly strong oxidising agents and this has been proposed as a reason for them inhibiting corrosion in deaerated solutions. Mechanisms proposed require adsorption followed by direct oxidation of the metal surface, chromate and nitrite both being oxidising agents with respect to iron. However, other strong oxidising agents e.g. permanganate and chlorate, show no tendency to inhibit corrosion at all. Certainly, the concentration of the anions is very important as nearly all anions at very low concentrations show aggressive behaviour, and at high concentration some aggressive species may be inhibitive\(^{52}\); a point made by Brasher\(^{52}\).

**Chromates**

Chromate has long been recognised as a very effective inhibitor particularly in cooling water systems. Its use is in decline, particularly in 'once-through' systems, because of its toxicity. The mechanism is not completely understood but the surface oxide has been shown to contain small amounts of chromium\(^{53}\). The mechanism is then one of ferrous ions being oxidised by chromate at the metal surface giving a ferric oxide layer with inclusions of chromic oxide. In practice chromate is a good inhibitor for a number of metals. It has been observed that after exceeding a threshold chromate concentration (7 x 10\(^{-4}\)M for steel wire)\(^{54}\) the corrosion rate falls dramatically. The inhibitor concentration may then be reduced
considerably with no adverse effect on the protected metal\textsuperscript{55}. Chromate is, however, like other anodic inhibitors, classed as dangerous. If the reaction is controlled completely by the anodic reaction then anodic inhibitors are fairly safe. However, when cathodic control, or mixed control, exists insufficient inhibitor leaves small anodic areas amongst large cathodic areas resulting in rapid pitting corrosion. Hence the addition of excess inhibitor at the commencement of treatment is a good practical precaution. Protection by chromate is reduced in aggressive environments, e.g. in high chloride concentrations\textsuperscript{55}. Molybdates and tungstates also act as corrosion inhibitors in the presence of oxygen\textsuperscript{50}, but are not as effective as chromates at equivalent concentrations and are relatively expensive. However, their toxicities are lower than chromate.

**Nitrite**

Nitrite is a good corrosion inhibitor in systems where pH is maintained above 6. The mechanism is not well defined but is generally considered to be similar to chromate in the sense that it is able to repair defects in the oxide film which is present in neutral solutions. In the absence of oxygen the nitrite itself acts as cathode reactant, increasing the mixed corrosion potential. Such a reaction would leave ammonia in solution and this has not experimentally been found. Adsorption of the inhibitor as an intermediate step has been proposed, on the basis of nitrite ion geometry in relation to the iron-iron metallic bond length\textsuperscript{56}, in formation of an iron oxide film at anodic areas. In practical applications nitrite has to be used at high concentrations (500 ppm - 1000 ppm) to be fully effective (insufficient inhibitor causes
severe pitting, as with chromate) but it does have good resistance to aggressive ions. In open systems it is particularly susceptible to bacterial decomposition, to nitrate, by nitrobacter agilis, which may lead to microbiological fouling. Biocides need to be added to the nitrite, making treatment expensive.

**Calcium carbonate**

Calcium carbonate precipitation may be used in corrosion inhibition if it is carefully controlled. It has been mentioned earlier that a thin carbonate layer can act as a cheap and efficient inhibitor but excessive deposition only serves to reduce heat transfer. The way in which the calcium carbonate is precipitated is important; a non-adherent sludge may promote corrosion rather than inhibit it. The Langelier index is commonly used to assess whether or not a water has the ability to form a protective carbonate layer. The index reflects the concentration of free carbon dioxide in solution, which is in equilibrium with carbonate compounds. With excess carbon dioxide in the water calcium carbonate deposition is not possible. The Langelier index calculates the pH of the water, for an equilibrium state of carbonate compounds, from chemical analysis of calcium and alkalinity:

\[ p\text{Heq} = p\text{Ca} - p\text{Alk} + (p_{k1} - p_{k2}) \]

where \( p\text{Heq} \) is the equilibrium pH value, \( p\text{Ca} = -\log[Ca^{2+}] \), \( p\text{Alk} = -\log \text{alkalinity (to methyl orange)} \), \( p_{k1} \) is the ionisation constant of \( \text{HCO}_3^- \) and \( p_{k2} \) is the solubility product of \( \text{CaCO}_3 \). Clearly \( p\text{Heq} \) varies with temperature. Langelier used the saturation index, S.I., to determine the stability of the water with respect to carbonates.

\[ \text{S.I.} = \text{pH} - p\text{Heq} \]

Where pH is the measured pH. Negative S.I.
indicates that the concentration of CO$_2$ is greater than the equilibrium concentration and the water is termed aggressive. Positive S.I. indicates that CO$_2$ is below the equilibrium concentration; the water is supersaturated with calcium carbonate, which can deposit onto a metal surface. Water treatment can be employed to obtain the desired saturation index (ideally +0.5 to 0.7). The pH has to be controlled between 6 and 7.5. In aggressive waters lime or sodium hydroxide may be added to increase the pH. If the calcium content is too low (below about 50 ppm) it will need making up. Excess CO$_2$ in the water can be removed by cascading or passing the water over crushed marble and dolomite. Increasing pH tends to reduce the CO$_2$ concentration, but beyond pH 7.5 excessive carbonate deposition occurs. Water velocity is important in depositing an adherent protective film, needing to be at least 0.8 ms$^{-1}$. Calcium carbonate tends to be deposited at cathodic sites where local pH is slightly greater than bulk solution pH. An insulating layer of carbonate reduces the rate of cathodic oxygen reduction. Enhanced pitting corrosion is not a problem with cathodic inhibitors as the anode area remains fairly constant whilst the corrosion current is reduced. This situation, however, is an over-simplification since experiments have shown a positive increase in mixed corrosion potential, suggesting a degree of anodic inhibition$^{59}$. 

**Silicates**

Silicates are occasionally used in once-through cooling waters and municipal potable waters where low toxicity is essential. Low doses are used, typically 4 to 10 ppm silicate for potable water systems$^{60}$ and 25 to 60 ppm as SiO$_2$ for cooling waters. The chemistry of silicates is rather complicated and this is particularly true in
aqueous solutions, where various ionic, molecular and complex forms exist. Silicates of the general form \( nNa_2O.mSiO_2 \) appear to have inhibitive properties which vary according to the m/n ratio. For mild steel a m/n ratio of 2.4 has been suggested for effective inhibition\(^6\). Doses below a critical level tend to accelerate corrosion\(^5\) and it is common practice to add an initial high dose of silicate to protect the metal completely, then lower the concentration to maintain protection. The initial film formation using silicate is slow compared with other inhibitors, making the initial high dose particularly important.

The mechanism of inhibition using silicates is not clearly established. It has been considered due to the increase of pH caused by the silicate, but this has been disproved\(^6\). A widely accepted mechanism is one of film formation by colloidal silicates depositing on the metal surface. A layer of iron oxide on the surface is beneficial to protection with silicates\(^6\), and, despite being classed as an anodic inhibitor\(^6\), it appears that a silica gel containing some iron species forms over the whole metal surface.

**Phosphates**

These are widely used as corrosion inhibitors in a variety of situations. Their low toxicity makes them popular in potable waters and once-through systems. Phosphates used as inhibitors are either ortho-phosphates or poly-phosphates; the mechanism of inhibition being different for each type. Ortho-phosphates of the type \( M_3P_4O_{10} \), where M is a monovalent cation, show inhibitive properties, but \( NaH_2PO_4 \) is not very effective, particularly at high concentration (greater than 0.5% w/v), due to fall in solution pH as a result of
hydrolysis. The inhibitive effect of ortho-phosphates are in the series \( \text{Na}_3\text{PO}_4 > \text{Na}_2\text{HPO}_4 > \text{NaH}_2\text{PO}_4 \) which correlates with the pH each creates in solution. This has been suggested as the reason for inhibition, but as with silicates the phosphate greatly assists in inhibiting dissolution, as demonstrated by detection of phosphates in the surface film\(^{65}\). The amount of phosphate present decreases with increasing pH. Oxygen is necessary for the phosphate to be effective so a film repair mechanism is envisaged\(^{50}\). A surface film of ferric oxide is formed and at anodic areas, where dissolution is occurring, ferric phosphate is deposited which plugs gaps in the film. The ortho-phosphates are thus considered to be anodic inhibitors.

Polyphosphates are difficult to define precisely as they often have variable chain lengths. Classification is best done by the molar ratio of \( \text{Na}_2\text{O} \) to \( \text{P}_2\text{O}_5 \), similar to the classification of silicates. These mole ratios, \( \text{Na}_2\text{O}:\text{P}_2\text{O}_5 \), vary from about 1.1 to 1.5. In practice doses vary between 2 and 100 ppm, as \( \text{PO}_4 \), according to situation, but for cooling towers 10 to 25 ppm is common\(^{66}\). Film formation and protection are achieved between 4 and \( 99^\circ\text{C} \) and down to \( \text{pH} 5 \)\(^{67}\), making it a versatile inhibitor. The rate of film formation is dependent upon diffusion of phosphate to the metal so steady flow is important and a high initial dose is useful to establish protection. Once protected in a polyphosphate solution the structure can remain so for as long as 14 days even in the absence of inhibitor\(^{68}\), which is useful if inhibitor supply stops for any reason. Polyphosphate requires oxygen to be effective, though in the presence of calcium the critical oxygen concentration for inhibition is lowered\(^{69}\). Calcium or magnesium ions in solution are essential for satisfactory inhibition with polyphosphates. The mechanism appears to result from deposition
of a film at the cathode. The detection of iron in the protective film does however suggest an effect on anodic dissolution reaction. Polyphosphates have good resistance to chloride ions and at high concentrations (above 0.4%) can protect mild steel in sea water. A further advantage of phosphates is their combination with calcium in forming an inhibitive film reduces calcium carbonate scale formation. This is used to advantage in boiler waters, but careful control must be exercised to prevent the build up of phosphate sludge.

**Benzoate**

Sodium benzoate, C₆H₅ COONa, is quite a well known inhibitor for steel and some non-ferrous metals. In solutions up to about 80°C and pH between about 5.6 and 8 a benzoate concentration of about 10⁻³M affords mild steel good protection, though it is rather sensitive to aggressive ions (chloride, sulphate and nitrate). Sodium benzoate is not a strong oxidising agent and it does not form insoluble iron salts. Benzoate only operates as an inhibitor in the presence of oxygen. The mechanism of inhibition is considered to be the combined effects of bonding the benzoate anion to the iron, via the carboxyl groups, with the oxygen present in solution passivating remaining active iron atoms. This is supported by the observation that by roughening the surface, for example by shot blasting, a correspondingly high concentration of benzoate is required to passivate the surface, compared to a polished surface.
**Borate**

Borates are not widely used on their own as inhibitors. It seems that their main effect as inhibitors is due to their buffer capacity in maintaining an alkaline pH. However, at high concentrations (>0.1M dm⁻³) it has been suggested that borate acts as an anodic inhibitor.⁶¹

**Organic Inhibitors**

This broad classification may be applied to inhibitors which are used in acidic solutions and particularly in acid pickling of steels for removal of mill scales. The greatest difference, with regard to the metal surface, between acid and neutral solution, is the absence or presence of a surface oxide film. In acid, where an oxide-free surface exists, adsorption of inhibitor molecules is an essential prerequisite for corrosion inhibition. The two major factors likely to influence adsorption of molecules onto a metal surface are a) the surface charge on the metal, determined with respect to the point of zero charge, and b) the functional group and structure of the inhibitor molecule. The point of zero charge of solid metal electrodes is not readily determined. However, if the surface charge of the metal is positive with respect to the point of zero charge anions are most likely to be adsorbed, and vice versa. The difference in surface charge on iron and mild steel has been proposed as the reason for their contrasting behaviour towards acid pickling inhibitors.⁷³ Structure and functional groups are important because many organic inhibitors bond directly to the metal surface by electron transfer. Thus, a molecule with loosely bound electrons e.g. delocalised π-electrons in aromatic compounds, or functional groups containing oxygen, nitrogen,
sulphur or phosphorous, which may have lone pair electrons for bonding, are particularly likely to be adsorbed. Experimental evidence has been obtained for organic compounds with different nucleophilic substituents, which strongly suggests that increasing electron density at the functional groups increases adsorption and results in greater inhibition. The adsorption of organic molecules is generally considered to block diffusion of both reactants and products at the electrode surface. Generally larger molecules form effective barrier films which prevent diffusion of reactants to and from the surface. Iron atoms which are bonded to organic molecules are not available for other reactions, and using this idea inhibition efficiency should increase with increasing inhibitor concentration. This is very often the case. Organic inhibitors may be anodic, cathodic or mixed types depending on their adsorption mechanism and subsequent reactions e.g. acetylenic groups are able to polymerise, after adsorption, covering the whole surface. The relationship between surface coverage (corrosion rate) and inhibitor concentration often follows a well defined adsorption isotherm.

Organic inhibitors commonly used for pickling of steel include hexamine, thiourea and derivatives and quinoline and derivatives. Inhibition improves with increasing concentration but near 100% coverage is achieved at about 0.1 mole dm⁻³.

Inhibitor Combinations

In practice inhibitor materials are rarely used alone, but rather combined with other materials. The resulting mixtures often display an advantageous synergistic effect. An early inhibitor of
this type was the mixture of chromate and phosphate, which was found to eliminate the pitting behaviour exhibited by chromate alone\textsuperscript{77}. The use of polyphosphate rather than ortho-phosphate further improves the inhibitor particularly at lower concentrations. This improvement results from combined anodic and cathodic inhibition, afforded by the individual materials. Care has to be taken in combining inhibitors to ensure that the components do not react with each other, particularly if one is a strong oxidising agent. Modern inhibitor formulations often contain amino phosphonates, though these are often made quite complicated by being heavily substituted. The substituents are important particularly with long chain alkyls or other bulky groups being substituted onto nitrogen atoms, preventing approach of the nitrogen to the metal surface. Phosphonates are reportedly cathodic inhibitors for ferrous metal corrosion\textsuperscript{78}, having a mechanism similar to that of polyphosphates. Experimental evidence has been presented suggesting that N,N-di-(phosphonomethyl)methylamine, in combination with nitrite, acts as an anodic inhibitor by a film repair mechanism as anodic sites, having no effect on the cathodic reaction\textsuperscript{79}. A review of patent literature\textsuperscript{80}, gives an idea of the considerable number and variations of inhibitor combinations which have successfully been used.
5. EXPERIMENTAL EQUIPMENT AND PROCEDURES

Electrolytic cell.

The cell used for all impedance work was a three arm cell with an added nitrogen lift pump and charcoal arm, for the purification of electrolytes, (Fig. 5.1). PTFE taps were fitted to isolate the charcoal arm prior to making small additions of materials to the electrolyte. The reference compartment was joined to the working compartment via a liquid film of high resistance around a partially closed PTFE tap. This prevented problems of electrolyte leakage previously encountered with ground glass taps. The working electrode and counter electrode compartments were separated by a glass frit. Each of these compartments had a glass tube with frit attached so that the electrolyte could be purged of oxygen.

The charcoal used for cleaning the electrolyte was prepared by two soxhlet extractions.

The first extraction, using 50% v/v hydrochloric acid, was to remove metal ions, especially iron from the charcoal. This was continued until the acid appeared colourless, typically after about six months. The acid was changed monthly. The second extraction, with tri-distilled water, removed chloride and hydrogen ions from the charcoal, and was continued until a silver nitrate test for chloride was negative. This again was typically six months, with monthly water changes.

The cell used for obtaining faradaic current data was a standard glass three arm cell, with the reference electrode joined to the working electrode via a Luggin capillary. All electrolytic
FIGURE 5.1. SCHEMATIC DIAGRAM OF THE ELECTROLYTIC CELL FOR CAPACITANCE MEASUREMENT.
Cells were cleaned prior to use by soaking in a 50:50 v/v mixture of nitric and sulphuric acids for at least five days. This was followed by several washings with tri-distilled water, and two washings with 1M NaClO₄. The cell was then filled with 1M NaClO₄, ready for use.

Electrodes

Working Electrode

The two materials used for working electrodes were:

1) Pure iron wire (99.999%), supplied by Johnson-Matthey Chemicals Limited, of 2mm diameter,

2) Mild steel wire, analysis, Carbon 0.041%, manganese 0.35%, sulphur 0.02%, phosphorous 0.023%, of 1.8mm diameter. The analysis of this wire is comparable with steel coupons used in industrial laboratory corrosion tests, which conform to BS 1449 part 1B.

One end of each wire was polished on 1200 grit emery cloth followed by 3/50 grade alumina, degreased in acetone, then immediately sheathed in polyethene. The polyethene was applied as a powder which was fused to the wire with a radiant heat source. The wire was then placed in a glass tube, this also being heated and bonded to the polyethene sheath. The flat face of the wire was exposed by cutting the polyethene. The metal was then polished on 1200 grit emery paper followed by alumina on a "selvyt" polishing cloth. These electrodes were found to suffer from leakage of electrolyte between the polyethene and wire. This effect is undesirable and in order to eliminate it two other methods of electrode preparation were employed.
First, the wires, after polishing and degreasing, were set in epoxy resin and left to harden.

Second, the wires were fitted into drilled teflon cylinders. The cylinders were drilled under size to make a tight push fit for the wire.

Of these two, the teflon sheath was used regularly as it was found quite satisfactory.

Counter electrode

The counter electrode was a rolled platinum gauze of large surface area (projected gauze area 19 cm²).

Reference electrode

The reference electrode used was a saturated sodium chloride calomel electrode (E = 0.236V). Sodium chloride replaced the potassium chloride supplied in the electrode, to avoid precipitation of KClO₄ in the ceramic junction. The ceramic junction was 1mm in diameter with a quoted electrolyte leakage of 0.1ml per 24 hours (25°C 1m w.g. pressure) [Pye Unicam reference electrode, catalogue number 303].

Electrolyte solutions

The experiments were carried out in 1M NaClO₄ (A.R. grade) solutions in tri-distilled water. At this high concentration NaClO₄ is totally dissociated. The perchlorate anion has the advantage that it is not adsorbed under the experimental conditions and there is no evidence of it enhancing or inhibiting corrosion.
The experiments were carried out at near neutral pH's which are most relevant to industrial systems. Solution pH was adjusted by dropwise addition of perchloric acid or sodium hydroxide, and monitored by a combined glass and reference electrode (EIL 1160) and pH meter (Fisons PTI 55).

Calcium ions were added to the system from a stock solution of 1M calcium perchlorate (Ventron Chemicals 99+%) in tri-distilled water.

Bicarbonate was added from a stock solution of 0.5M sodium bicarbonate (A.R. grade) in tri-distilled water.

Phosphate was added from a stock solution of 0.5M sodium dihydrogen ortho-phosphate in tri-distilled water.

**Electrical Circuits and Measurements**

**Faradaic current-potential data**

These data were obtained using a Kemitron POT 03 potentiostat. Cell current was measured using an ammeter present within the potentiostat. Data were obtained by allowing a clean electrode to equilibrate with the electrolyte at -1200 mV before measuring the cell current. The potential was shifted in 100 mV steps every 2 minutes, making a current measurement at each potential.
Impedance Measurements

Electrode impedance was measured, as a series resistance and capacitance, using a Schering bridge (Fig. 5.2) which was constructed from Muirhead 0.1% grade components. The accuracy of the bridge over the frequency range used (105Hz - 10kHz) was ±5% when tested with standard resistors and a 1μF capacitor (0.1%). This was in agreement with Larkin⁸² but it was noticed that at high frequency, the accuracy of measurement of capacitance deteriorated with increasing series resistance.

The A.C. signal (Brookdeal signal source 9471) was set, using an oscilloscope (Advance OS 2200), to 7.5 mV peak to peak after passing through the 65:1 step down transformer. The signal from the bridge was passed through a tunable filter (Muirhead D-925-B) set to eliminate 50Hz mains interference. The remaining signal was detected by a tuned amplifier (General Radio 1232A) with a sensitivity of 1μV full scale deflection.

The electrode potential was set by polarising the bridge symmetrically using a 6 volt battery via a potentiometer. Electrode potential was monitored against a saturated sodium calomel electrode with an electrometer (Keithley 610 B). The working electrode was connected to earth to avoid screening difficulties. The a.c. and d.c. components were separated with a 40H choke.

When the bridge is balanced \[ C_{se} = \frac{C_4 R_2}{R_1} \]

and \[ R_{se} = \frac{R_1 C_2}{C_0} \]

The values of the series resistance, \( R_{se} \), and capacitance, \( C_{se} \), of the electrode are readily obtained using the Schering bridge.
A.C. BRIDGE CIRCUIT

G - Digital ammeter
Electrode capacitance - potential data were obtained by allowing the electrode to equilibrate with the electrolyte at -1100 mV for thirty minutes. The series capacitance and resistance were measured at 1kHz, a new potential set and the bridge balanced again almost immediately.

The capacitance of the electrode was also obtained over a frequency range of 105Hz to 10kHz at constant potential. The potentials selected were -1100 mV, -800 mV, -600 mV and 1000 mV. Electrodes were held at the appropriate potential for thirty minutes before making capacitance measurements. Exact multiples of 50Hz were avoided, particularly at low frequencies.

Additional impedance data were obtained using a Solatron 1172 frequency response analyser (F.R.A.) and a Solatron 1186 electrochemical interface (Fig. 5.3). The main advantage over the bridge method is the ability to obtain much useful information below 100Hz.

The Solartron equipment has a programmable signal generator which provides the perturbing signal, then the F.R.A. measures the response of the system under test, analyses it by a correlation process then displays the result.

The generator may be programmed to measure responses at one frequency or more commonly over a range of frequencies (as wide as 10kHz to 1mHz), at a variable number of measurements per frequency decade (ten in the present study). These intervals are equally spaced on a logarithmic scale. The perturbing signal amplitude is programmable, and set at 3 mV R.M.S. for this study. The response of the system can be displayed in one of three modes; amplitude and phase angle (relative to the output signal), log amplitude and
FIG. 5.3

CELL IMPEDANCE MEASUREMENT SYSTEM.
phase angle or as the real and imaginary parts of the test system's impedance. The latter mode was used exclusively. Results were transferred (via a Solatron 1180 data transfer unit) onto a tape punch/teletype machine. The plotter interface displayed data via a Bryans 26700 X-Y recorder. Punched tapes were filed on the University's Prime 400 computer and analysed using specially developed software.

The Solatron 1172 F.R.A. correlates the response of the cell with two synchronous reference signals; one in phase with the perturbing signal and one $90^\circ$ out of phase with the perturbing signal. The technique has the advantage of rejecting all harmonics, only measuring the fundamental response. Random noise in the system is only eliminated with an infinite integration time. In practice the complete elimination of random noise is not possible but with integration over a fairly large number of cycles the bandwidth may be reduced sufficiently to greatly lessen the effects of noise.

In this study integrations over 10 cycles, and 1 cycle at low frequencies (below about 100mHz) were used to obtain acceptable data as quickly as possible.
6. RESULTS AND DISCUSSION

Faradaic current-potential curves

All potentials in the present work are expressed with respect to the saturated sodium calomel electrode (E = 0.236V). Faradaic current-potential data are shown for both iron and mild steel in Figs. 6.1 and 6.2. Both curves show the frequently observed behaviour exhibited by these materials. Both show an apparently polarisable region between -1100 mV and -600 mV, after which current rises rapidly. Mild steel has a higher maximum current than pure iron, which is to be expected due to the greater heterogeneity of the steel surface. Further anodic polarisation induces passivity. The exact potential at which this occurs has not been noted, but the dramatic fall in current is clearly visible for both iron and mild steel. The potential range from -1200 mV to 1100 mV is therefore accessible for study using capacitance measurements in neutral solutions.

The potential of zero charge on iron

Impedance data for an iron electrode in borate buffer solution (pH 8.7) has been published. From this it was concluded that in borate buffer a fast faradaic process exists between -900 mV and -700 mV (Hg/HgO in 4.35M KOH, E = 0.0984V), with film formation in evidence at the anodic end of this region. The capacitance minimum observed at -1050 mV (Hg/HgO) was not associated with the p.z.c. of iron, but was considered a convolution of pseudo-capacitances for iron dissolution on the anodic side and hydrogen evolution of the cathodic side of -1050 mV.
FIG. 6.1

FARADAIC CURRENT Vs POTENTIAL
IRON 1M NaClO₄ pH7
FIG. 6.2

FARADAIC CURRENT Vs POTENTIAL
MILD STEEL 1M NaClO₄ pH 7
Any study of inhibitors, particularly adsorption types, make a knowledge of the p.z.c. important\textsuperscript{83}. Thus the present results are used here to verify previous work, and establish that the p.z.c. of iron and mild steel are not attainable in a neutral, inert electrolyte.

**Differential capacitance - potential curves and the parallel transformation**

Capacitance-potential curves are shown for iron and mild steel in the base electrolyte at pH 7 in Figs. 6.3 and 6.4.

They support the earlier observation that, as expected, mild steel is more active in dissolution than iron. Otherwise, the two graphs are of the same shape, showing a peak at about -250 mV. The minimum observed at about -600 mV is common to both materials. This is the region for which the p.z.c. is a distinct possibility\textsuperscript{18}. This possibility was examined by transforming the series electrode impedance components to a parallel combination (as shown earlier). Plots of the parallel capacitance, \( C_p \), against \( \omega^{-1} \) should be straight lines, giving \( C_L \) at infinite frequency, for a faradaic process if the diffusion in solution is the main control over the frequency range used.

The experimentally polarisable region was explored using this technique. Typical plots are shown in Figs. 6.5 and 6.6. (Other pH values around 7 were also examined by this technique, the results of this are included for completeness in Figs. 6.7 to 6.10). It is seen that satisfactory lines were obtained for all cases examined. Any gross curvature of the plots (e.g. iron in pH 8 electrolyte) is attributed to adsorption, probably of an intermediate species in the dissolution reaction.
FIG. 6.3

IRON 1M NaClO₄, pH 7
FIG. 6.4

CAPACITANCE Vs POTENTIAL

MILD STEEL 1M NaClO₄ pH7

\[ C_{Se} / \mu \text{Fcm}^{-2} \]

\[ E/\text{mV} \]
FIG. 6.5
PARALLEL CAPACITANCE Vs $\omega^{-1/2}$
IRON 1M NaClO$_4$, pH7

$C_p / \mu F/cm^2$

$\omega^{-1/2}$ / $s^{1/2}$
FIG. 6.6
PARALLEL CAPACITANCE Vs $\omega^{-1/2}$
MILD STEEL 1M NaClO₄ pH 7

$C_p/\mu Fcm^{-2}$

$\omega^{-1/2} $ vs $S^{1/2}$

- 600 mV
- 400 mV
- 200 mV
- 100 mV
- 50 mV
- 25 mV
- 10 mV

0.01 0.02 0.03 0.04
FIG. 6.8

Mild Steel. 1M NaClO₄, pH 8
FIG. 6.9

Iron. 1M NaClO₄, pH 8

\[ E \text{ vs. } \frac{\omega^{-1/2}}{S^{1/2}} \]

-600 mV

-1100 mV

-800 mV

1000 mV
FIG. 6.10

Mild Steel, 1M NaClO₄, pH 8

Cp, µF/cm² vs. \( \frac{\omega^{1/2}}{5^{1/2}} \)

-1100 mV
-800 mV
-600 mV
1000 mV
Capacitance-potential data obtained for each electrode with additions of natural water constituents, calcium and bicarbonate, and an inhibitor, ortho-phosphate are presented in Figures 6.11 to 6.16. All graphs show a peak occurring at about the same potential (around -300 mV). The magnitude of the peaks for iron are fairly consistent, though peak broadening and slight cathodic shift is observed when all additions are made. With mild steel the peak position is fairly constant, but a considerable fall in capacitance occurs with addition of bicarbonate and a further decrease with addition of phosphate.

It can be concluded from the data that the p.z.c. of iron is not attainable in neutral, inert electrolyte under the conditions employed in this study.

Impedance diagrams in the complex plane

Pure Iron

It was previously noted that considerable work has been carried out on the dissolution of pure iron in acidic solution. (It is clear from this work that there are a number of steps involved in iron dissolution). Previous d.c. experiments have elucidated mechanisms with a single rds, but the use of a.c. impedance methods, over a wide frequency range, has brought about proposals for more than one kinetically hindered step within the overall dissolution mechanism84,85.

The present study has been concerned with neutral solutions (at about pH 7), which are industrially relevant to water treatment. The ohmic resistance has been overcome by the addition of a high concentration of inert electrolyte (this will also swamp any
FIG. 6.11

CAPACITANCE Vs POTENTIAL

IRON 1M NaClO₄  100ppm Ca²⁺ pH 7
FIG. 6.12

CAPACITANCE Vs POTENTIAL

IRON 1M NaClO₄ • 100 ppm Ca²⁺ • 100 ppm HCO₃⁻ pH 7

Cₛₑ / µFcm⁻²

E / mV

-800 -400 0 400 800 1200
FIG. 6.13

CAPCITANCE Vs POTENTIAL

IRON 1M NaClO₄ + 100ppm Ca²⁺ + 100ppm HCO₃⁻ + 10ppm PO₄³⁻ pH 7

C_{se} / pFcm²

E/mV

-1200  -800  -400   0   400   800  1200
FIG. 6.14

MILD STEEL

1M NaClO₄ + 100ppm Ca²⁺ pH 7

\[
\frac{C_{SO_4}}{\mu Fcm^{-2}}
\]

\[
E / mV
\]
FIG. 6.15

CAPACITANCE Vs POTENTIAL

MILD STEEL 1M NaClO₄ + 100 ppm Ca²⁺
+100 ppm HCO₃⁻ + 10 ppm PO₄³⁻ pH 7
FIG. 6.16

CAPACITANCE Vs POTENTIAL

MILD STEEL 1M NaClO₄ 100 ppm Ca²⁺ 100 ppm HCO₃⁻ pH 7
complicating double layer effects). Pure iron, under the present experimental conditions, has a fairly simple impedance behaviour. The complex plane plot is very similar to that expected for a charge transfer reaction and diffusion in solution, i.e. a semi-circle at high frequencies going off into a Warburg line at about 45° to the real axis, Figs. 6.17 to 6.21. A comparison of data from the present study with others\textsuperscript{84,85} is complicated by the inclusion of the Warburg diffusion in the present results. (The experimental arrangements employed here did not allow suppression of Warburg effects). It is possible, in the majority of cases, to superimpose the results cited above onto a line at 45° to the real axis. The impedance behaviour of iron particularly at about -400 mV has not shown any capacitive or inductive loops at low frequency, as reported by Keddam et al and Schweickert et al. This must be attributed to the difference in experimental techniques already mentioned and suggests overall rate control by diffusion with rapid formation and reaction of intermediates.

The present impedance data is coincident with the proposals of Kabanov et al\textsuperscript{19} and Bockris et al\textsuperscript{25} whose mechanisms have a single rds involving charge transfer preceded by a rapid adsorption and followed by rapid dissolution.

The impedance behaviour is fairly consistent, but does show a degree of potential dependence. At high cathodic potentials (-1100 mV and -800 mV) the dihedral is at about 45°. At -600 mV interesting behaviour is observed with the dihedral rising sharply and considerably steeper than 45°. This may be attributed to adsorption of a species which increases the electrode pseudo-capacitance due to the potential dependence of the adsorption isotherm. Further increase in potentials lowers the dihedral.
FIG. 6.17

IRON 1M NaClO₄
pH7-1100mV

$J_{WC \text{ Ohm}}$

$R/\text{Ohm}$

0 500 1000 1500 2000 2500
FIG. 6.18

IRON 1M NaClO₄
pH7 -800mV

1/\omega C Ohm

R/Ohm

0 1000 2000 3000 4000 5000
FIG. 6.20

IRON 1M NaClO₄
pH7 -400mV

\[ R_{\text{Ohm}} \]

\[ \frac{1}{WC \text{ Ohm}} \]

0 700 1400 2100 2800 3500

0 100 10 8
FIG. 6.21

IRON 1M NaClO₄
pH 7 1000 mV

1/\omega C (\Omega m)

R/\Omega m (x10³)

0 7 14 21 28 35
At 1000 mV the dihedral is well below 45° and at this potential a passive film of considerable thickness will very likely cover the surface. The anodic passivation of the surface by external polarisation is of no relevance to the present study. The results obtained at -400 mV and -600 mV show signs of a second semi-circle forming at frequencies below about 1Hz. This effect is almost certainly due to convective diffusion becoming important at low frequencies, in agreement with Epelboin et al\textsuperscript{15} this is more significant at potentials at which relatively high current flows as a consequence of a small change in the potential.

**Mild Steel**

The impedance loci for mild steel under the same conditions used for iron are shown in Figs. 6.22 to 6.26. All but one of these plots show similar behaviour to those seen for iron i.e. a high frequency semi-circle which develops into a line at about 45° at lower frequencies. This Warburg slope indicates ultimate reaction control by diffusion.

The shapes are not as well defined as those for iron, and is complicated at -400 mV by the loss of Warburg tail. It was decided that this potential is where the dissolution reaction is most readily investigated (discussion of this follows later).

Generally, the same conclusions can be drawn for the electrode reactions at mild steel as were drawn for pure iron.

**Mild Steel in the active region**

Figs. 6.27 and 6.28 show the Randles presentation of impedance data (which include the double layer i.e. the real
FIG. 6.22

MILD STEEL 1M NaClO₄
pH7-1100mV

1/\omega C Ohm
(x10³)

R/Ohm (x10³)
FIG. 6.23

MILD STEEL 1M NaClO₄
pH7 - 800mV

1/\omega C, Ohm
(x10³)

R/Ohm(x10³)
FIG. 6.24

MILD STEEL 1M NaClO₄
pH7 -600mV

\[ \frac{1}{W} \text{C Ohm} \]

\[ R/\text{Ohm} \times 10^3 \]

\[ 1/\text{W} \times 10^3 \]

\[ R/\text{Ohm} \times 10^3 \]
FIG. 6.25

MILD STEEL 1M NaClO₄
pH 7 -400mV

\[ \frac{1}{\omega C} \text{Ohm} \]

\[ R/\text{Ohm} \]
FIG. 6.27

MILD STEEL 1M NaClO₄ + 100 ppm Ca²⁺ + 100 ppm HCO₃⁻ + 10 ppm PO₄³⁻ NO AIR

pH 7 - 400 mV
FIG. 6.28

MILD STEEL 1M NaClO₄ + 100 ppm Ca²⁺ + 100 ppm HCO₃⁻ + 10 ppm PO₄³⁻ + AIR

pH 7 - 400 mV

Omega = (1/2)

R & 1/wC Ohm

0.00 0.80 1.60 2.40 3.20 4.00

Omega = (1/2)
and imaginary part of the total electrode impedance).

The shapes obtained are extremely complicated and cannot be interpreted using the classical methods of Randles$^6$, Laitinen and Randles$^8$, and Farr and Hampson$^9$. These shapes are typical of those obtained in this study for mild steel at $-400 \text{ mV}$ both with and without additions.

Discussion of impedance data using the Sluyters complex plane presentation simplifies further analysis of the results. Keddam et al, following work of Epelboin and co-workers, gives perhaps the most advanced discussion of iron electrode reactions from impedance data. In view of the present, rather limited investigation (due to time), the Sluyters representation will be used in providing a qualitative explanation of behaviour encountered.

The faradaic current curve for mild steel shows a highly active region at about $-400 \text{ mV}$. The magnitude of the current in this potential region is considerably greater than those for iron under corresponding conditions. This interesting difference is to be expected and has been commented on already in some detail.

An interesting feature of this active dissolution region is the effect of the alloying components on the impedance spectrum of mild steel. This is shown in Fig. 6.25. Compared with other impedance spectra of mild steel at other potentials, the spectrum obtained at $-400 \text{ mV}$ has a lower resistive and capacitive component, in keeping with a faster dissolution reaction. Within the experimental range the Warburg effect is not seen. At the low
frequency end of the elongated semi-circle the ohmic resistance decreases with an increasing capacitive component, and then an apparent return to the real axis occurs towards zero frequency.

Similar shapes to this have been discussed by Epelboin et al\textsuperscript{15,16} for the passivation of iron with coupling of diffusion kinetics.

Qualitatively, we can interpret the impedance spectrum as a rapid dissolution involving adsorbed intermediates at the electrode. At high frequencies the concentration of intermediates is unaffected by the negative going cycle of the a.c. because the relaxation time associated with them is too long. As the frequency is lowered the intermediates can discharge during the negative cycle of the a.c., and negative current can be fed back into the reaction as a consequence of this. This results in a decrease of the effective in phase resistance and an increase in capacitance. At zero frequency the locus would be expected to return to the real axis. However, Fig. 6.25 shows some evidence, albeit in a small, random manner, for solution diffusion at the lowest experimental frequency available. The most likely intermediate, on evidence provided by Epelboin and co-workers, is $[\text{Fe(OH)}_2]_{\text{ads}}$.

It is of interest to note that their experimental impedance diagrams return to the real axis in a satisfactory manner as a consequence of removing the Warburg by employing a rotating disc electrode (at about 750 R.P.M.).

It can be concluded from the present work in the active dissolution region of mild steel that at high rates of electrode dissolution there is a tendency for passivation with precursory
adsorption of an intermediate species, probably Fe(OH)$_2$.

This interesting adsorptive behaviour was not observed on iron, possibly because the lower rate of reaction at pH 7 was inadequate to produce the necessary electrode conditions, and, as mentioned, diffusion processes are dominant.

The effect of natural additives

Iron

Figs. 6.29 to 6.32 show the effect of additives on the impedance spectra of iron in 1M NaClO$_4$ electrolyte at -400 mV.

The addition of 100 parts per million of calcium (as Ca(ClO$_4$)$_2$.6H$_2$O) has very little effect on the impedance spectrum, neither the shape nor magnitude of the plots being significantly different to those in base electrolyte.

The addition of 100 p.p.m. of bicarbonate (as NaHCO$_3$), which renders the system analogous to industrially encountered conditions appears to retard the kinetics slightly. The form of the impedance spectrum is essentially the same, with the exception of the Warburg tail, which has a lower dihedral. This may be explained by the formation of a thin film of calcium carbonate at the electrode, particularly at centres of dissolution. This lower dihedral can be interpreted as porosity, or heterogeneity associated with a two phase surface.

Addition of phosphate (as NaH$_2$PO$_4$.2H$_2$O) at a level of 10 p.p.m. (corresponding to a typical dosage in cooling water systems) the complex-plane plot shows a fairly unreactive system in which the double layer capacitance is low. The Warburg tail is at an angle
FIG. 6.29

IRON 1M NaClO₄+100 ppm Ca²⁺

pH 7: -400 mV

1/WC Ohm

R/Ohm
FIG. 6.30

IRON 1M NaClO₄ + 100ppm Ca²⁺ + 100ppm HCO₃⁻

pH 7 - 400mV
FIG. 6.31

IRON 1M NaClO₄ + 100 ppm Ca²⁺ + 100 ppm HCO₃⁻ + 10 ppm PO₄³⁻ NO AIR
pH 7 - 400 mV
FIG. 6.32

IRON 1M NaClO₄ + 100ppmCa²⁺ + 100ppmHCO₃⁻ + 10ppm PO₄³⁻ • AIR

pH 7 -400mV
close to the theoretical $45^\circ$, suggesting a less heterogeneous surface. This may be caused by a more uniform film arising from the inhibitive properties of phosphate. It is interesting to note here that there is little difference between the data for additions of phosphate in the absence and presence of oxygen. The main difference is the increase in the dihedral in the presence of oxygen, where it is very close to the theoretical $45^\circ$ for a planar electrode. The increase in dihedral observed here may be interpreted as further consideration of the surface film and repair of defects in this thin film by phosphate in the presence of oxygen. Such behaviour is in keeping with proposed mechanisms for the inhibitive mechanism of ortho-phosphates.

The data presented demonstrate that carbonate and phosphate are able to inhibit the dissolution of iron, with some evidence available to support a surface film defect repair mechanism by phosphate in the presence of oxygen. Quantitative data on the degree of inhibition is not readily obtained from the present data.

This is by no means a new observation since highly purified water is known to engender a more rapid corrosion rate than tap water.

**Mild Steel**

Figs. 6.33 to 6.36 show the effect of additives on the impedance spectrum of mild steel in 1M NaClO$_4$ electrolyte at $-400$ mV.

Addition of 100 p.p.m. of calcium generates an inductive semi-circle, at low frequencies, followed by a second capacitive semi-circle in the real plane. Such impedance loci are relatively
FIG. 6.33

MILD STEEL 1M NaClO₄ + 100 ppm Ca²⁺
pH 7 - 400 mV
FIG. 6.34

MILD STEEL 1M NaClO₂+100ppmCa²⁺+100ppmHCO₃⁻
pH7 -400mV

1/\omega C Ohm

-20     0      20  40  60  80  100  120
R/Ohm
FIG. 6.35

MILD STEEL 1M NaClO₄ +100 ppm Ca²⁺, 100 ppm HCO₃⁻, 10 ppm PO₄³⁻ NO AIR
pH 7 -400 mV

1/ \omega \, \text{Ohm}

R/\text{Ohm}

-30

-20 50 80 110 140 170

120

90

60

30

20 10000

1000

100
FIG. 6.36

MILD STEEL 1M NaClO₄ + 100 ppm Ca²⁺ + 100 ppm HCO₃⁻ + 10 ppm PO₄³⁻ + AIR
pH 7 -400mV

$\frac{1}{\omega C \text{ Ohm}}$

R/Ohm

-30 30 60 90 120 150 180

$\frac{1}{\omega C \text{ Ohm}}$

0 30 60 90 120 150 180

$\frac{1}{\omega C \text{ Ohm}}$
common at near-neutral pH, as a precursor to passivation. Such behaviour is only observed when the current is high, a point made by Keddam et al. These workers have discussed their results in terms of a reaction model in which two intermediate species are present.

\[
\begin{align*}
\text{Fe} & \xrightarrow{k_1} \text{Fe(I)ads} \xrightarrow{k_2} \text{Fe(II)sol} \xrightarrow{k_5} \text{Fe*(II)ads} \xrightarrow{k_7} \text{Fe(II)ads} \\
\text{Fe} & \xleftarrow{k_3} \text{Fe(I)ads} \xleftarrow{k_6} \text{Fe*(II)ads} \\
\text{Fe*(I)ads} & \xrightarrow{k_4} \text{Fe*(II)ads}
\end{align*}
\]

Here they are the Fe*(I)ads and Fe*(II)ads species. Qualitatively, each intermediate displays its own discrete loop in the impedance diagram. The theory behind the models of Keddam et al is very convoluted. However, it is clear from results of the present study that calcium stabilises a second adsorbed intermediate. Similar impedance diagrams are observed in solutions containing calcium and bicarbonate, and calcium, bicarbonate and phosphate. It is very difficult in this limited time study to speculate deeply on the identity of these intermediates.

The effect of oxygen in the system is to produce a loop in the real quadrant, removing the inductive component noted previously. Qualitatively, again, this effect could represent a change in balance of one adsorbed intermediate with respect to the other. Assuming the iron(I) intermediate to be more stable than the iron(II)
intermediate (a fair assumption as iron(I) is not in doubt, being the widely accepted first step, while iron(II) arises to satisfy the proposed theory of Keddam et al). The effect of oxygen appears to be lowering the iron(II) intermediate species concentration (the Fe(I)ads → Fe*(II)ads reaction giving rise to inductive impedance behaviour). Keddam et al demonstrated the generation of impedance loci, not dissimilar to those presented here, in terms of electrode coverage by different intermediate species.

The shapes given here for mild steel in the presence of oxygen are fairly similar to those obtained by Keddam et al at the corroding iron electrode at the onset of rising corrosion current, under comparable potential conditions. (The French workers used a saturated Hg/Hg₂SO₄ electrode at pH 5, so precise comparison of potentials is rather difficult). Their similar impedance plot shows a slight inductive region between 25Hz and 0.6Hz which correspond to the low point of the loop obtained from our data. As pointed out already the French workers suppressed Warburg effects, and in the present study the effect of the Warburg impedance would be to raise the whole of the impedance loci slightly, with the effect in this case of eliminating the inductive element.

It is reasonable to conclude that, in terms of the detailed study of Keddam et al, our results are in agreement with their mechanism V (reproduced earlier).

It must be noted that the addition of calcium, bicarbonate and phosphate does not appear to inhibit the steel dissolution, but there is evidence, just discussed, of changes in the interphase structure giving rise to changes in the electrode impedance.
We must conclude that in the limited potential range studied the effect of ortho-phosphate in the presence, and absence of oxygen is very limited with respect to the inhibition of corrosion of mild steel and iron.
1. The differential capacitance technique is useful for identifying the interfacial surface structure of iron and mild steel.

2. Differential capacitance results obtained in 1M sodium perchlorate indicate that the point of zero charge on iron may possibly be identified in some of the present experimentally accessible regions. However, frequency dispersion measurements made around the most likely potentials, when interpreted by a parallel transformation technique, proves that this cannot be justified and confirms that the point of zero charge is inaccessible under the present experimental conditions.

3. For steel electrodes the dissolution reaction in sodium perchlorate at neutral pH is faster than the corresponding dissolution of pure iron. This is interpreted on the established general principle that impure, heterogeneous metals corrode more rapidly than pure ones (in the absence of protective alloying ingredients e.g. chromium and nickel in stainless steels).

4. Impedance plots in the complex plane (Sluyters) have been useful in interpreting corrosion reactions of iron and mild steel in the base electrolyte and with addition of natural water constituents to this electrolyte. For an iron electrode in the presence of phosphate ions interesting behaviour was observed, with the dihedral of the Warburg tail of the impedance plot at low frequency increasing toward 45° in keeping with the
4. (Continued)

expectation that ortho-phosphates repair film defects. A repaired film being relatively smooth would give the observed near 45° slope (compared with lower slopes observed from electrodes with a rough, discontinuous surface film).

5. Mild steel under the present experimental conditions more actively corrodes and exhibits impedance behaviour identified for iron under active corrosion conditions by French workers. This appears to be connected with the impurity concept (conclusion 2): the impurities (in mild steel) transforming a very slow, simple corrosion reaction (on pure iron) to a much more rapid one.

6. Further work is being undertaken to investigate the specific effect of inhibitors based on polyphosphates, in natural waters with no supporting electrolyte. It is hoped that this will provide an insight into the mechanism and efficiency of this group of inhibitors. The investigation of other inhibitors, particularly phosphonates, and combinations of inhibitors is a long term aim.

7. It is considered that the impedance techniques are the most useful for indicating whether materials are potentially good inhibitors. It is also hoped, in future, to correlate impedance data obtained quite rapidly with the results of longer term coupon weight loss measurements and ultimately field trials, such work would be in co-operation with Dearborn Chemicals Ltd.
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