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Reducing of Iron Corrosion in Water Pipelines by Hydrogen Addition

Feraih Sh. Alenazey

**Thesis submitted to the
College of Engineering and Mineral Resources
At West Virginia University
in partial fulfillment of the requirements
for the degree of**

**Master of Science
in
Chemical Engineering**

**Alfred H. Stiller, Ph.D., Chair
Charter D. Stinespring, Ph.D.
Peter G. Stansberry, Ph.D.**

Department of Chemical Engineering

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ABSTRACT

Reducing of Iron Corrosion in Water Pipelines by Hydrogen Addition

Feraih Sh. Alenazey

In the Arabic Peninsula water is a scarce commodity. Water is provided to the citizenry of the Kingdom of Saudi Arabia by the desalination of seawater. This desalination is done primarily through distillation. The purified water is then transported through extensive pipelines to the cities where it is used. During the process of transport the water becomes polluted with soluble iron. The iron is the product of corrosion of the pipeline material. The pipelines are buried in about four feet of dry sand and since the sand is essentially non-conducting medium the traditional methods for corrosion control are not applicable. A different approach needs to be developed to reduce the pollution to a tolerable level so the water can be made acceptable to the citizenry.

The corrosion of iron in the pipelines is the result of an oxidation reduction reaction. In that reaction hydrogen ion is reduced and the iron is oxidized. The hypothesis of this thesis is that the electrochemical potential of the hydrogen half-cell reaction can be reduce by dissolution of hydrogen gas in the water. If that value can be reduced enough then the oxidation of iron will be thermodynamically forbidden. If that condition cannot be obtained, then reduction of the electrochemical potential of the hydrogen half-cell will reduce the rate of corrosion. If the reaction rate is slow enough, then by dilution the pollution will be insignificant. The objective of this research is to evaluate the effect of hydrogen infusion on the corrosion rate of iron.

There are traditional methods to evaluate corrosion rates but these apply to electrolytic solutions and distilled water does not fit that description. By experimentation the corrosion rate was evaluated and the critical parameters determined. The limiting value for the corrosion is controlled by the exchange current density of the hydrogen half-cell. This was shown to be $10^{-5.2}$ amps. This will reduce the corrosion rate of iron by an order of magnitude with respect to nitrogen infused water. The oxidation of iron in water cannot be eliminated by infusion with hydrogen at atmospheric pressure, but it is believed that by infusing hydrogen in water at higher pressure the corrosion reaction can be eliminated. Preliminary data support this hypothesis.

Dedicated to my family

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CHAPTER 1

INTRODUCTION

In the Arabian Peninsula water is a scarce commodity. The primary technology used currently to supply the citizens with pure water is distillation of sea water. The distilled water is then pumped through pipes to cisterns above the households where the water is available for use. During the transport of the water, it becomes distasteful and discolored because of high concentrations of iron. The iron concentration is believed to be the product of corrosion of the pipes through which the water is transported. These pipes are made of steel and are buried at a depth of 4 feet. The soil in which the pipes are buried is essentially dry sand. This creates a unique system where classical solutions to prevent corrosion may not apply. A unique approach to corrosion prevention needs to be developed. This technique should be able to eliminate the corrosion and subsequent iron contamination of the drinking water.

Corrosion is the reaction of a base metal with oxygen. The products of this reaction are metal oxides. The base metal is reacted with oxygen to produce metal oxides and the physical integrity of structures, manufactured from the base metal, is compromised. Classic chemistry, commonly represents reactions of this type in electrochemical terms. There is an oxidation reaction, in which the metal atoms lose electrons; and a reduction reaction, where atomic oxygen gains electrons. Electrochemical reactions can be expressed in thermodynamic terms [this will be discussed in detail later]. There is a specific voltage for every oxidation and reduction reaction at standard conditions. The voltage of half cells is determined by comparison to a standard voltage. The standard is the hydrogen oxidation. The voltage forcing a

chemical reaction is the sum of the potential for the oxidation half reaction and the reduction half reaction. Classical chemistry uses thermodynamic conventions to represent these types of reactions. If the voltages for the oxidation and reduction reactions are summed and the sum is positive, then the reaction will proceed in the direction it is written. If, on the other hand, the sum is negative, then the reaction will not go on the direction it is written but will go in the opposite direction. If the sum is 0, then the reaction is in equilibrium. In the literature review of this thesis, the complete discussion of half cell potential will be presented.

1.1 Desalination Plants in Saudi Arabia

The Kingdom of Saudi Arabia is considered the biggest producer of desalinated water in the world, contributing to 30 percent of global production. Its production capacity is more than two million cubic meters daily. This quantity is the product of 27 desalination plants situated at 15 locations on both eastern and western coasts of the Kingdom. Their locations are shown in the figure below:

FIGURE 1.1 Desalination Plants In Saudi Arabia.(1)

1.2 Desalination Methods used in Saudi Arabia

There are currently four major desalination processes used in Saudi Arabia:

- 1- Multi-Stage Flash evaporation (MSF)
- 2- Reverse Osmosis (RO)
- 3- Electro dialysis (ED)
- 4- Vapor Compression (VC)

The MSF process is used at more than 90 percent of all desalination plants in the kingdom.

1.3 Pipelines Transportation System in Saudi Arabia

The water pipelines network is very huge. It provides around 70% of the portable water needs of the major cities. The total length of pipelines used for the transmission of desalinated water is about 3722 km. Most of these pipelines are buried at a depth of 4 feet in the dry sand as it is shown in the following figure:

FIGURE 1.2 Transportation pipelines are buried in the dry sand.(2)

1.4 Objective:

The goal of this research is to control the corrosion of steel water pipelines by adjusting the solution potential so that oxidation is reduced to the point that the iron concentration in the water is negligible. The water would then have reduced soluble iron and be acceptable for household and industrial use. It is the hypothesis that the solution potential of the water can be reduced to meet the objective above by saturation the water with hydrogen gas at atmospheric pressure.

CHAPTER 2

LITERATURE REVIEW

2.1 Electrical Potential and Corrosion

2.1.1 Measurement of electro chemical potentials:

All corrosion reactions are oxidation and reduction reactions. Before any knowledge of corrosion can be appreciated some basic definitions need to be established. Electrons are lost by the metallic species and electrons are gained by the nonmetallic component. When an atom loses electrons, it becomes a charged species or an ion. Because there are now more protons than electrons it assumes a positive charge. The atom that loses electrons is oxidized. Oxidation results in the production of a positive ion. Similarly, the agent that gains electrons has more electrons than it has protons so the ion produced becomes negative with respect to the original species. It is reduced. The metallic species that caused the reduction of charge to its complementary reactant is called the reducing agent. Thus the oxidized species is the reducing agent. Similarly, the agent that gains electrons and is reduced causes the metallic species to lose electrons. Thus the reduced species is called the oxidizing agent. In solution the negatively charged ions are called anions. Anions are attracted to a positively charged electrode where they can give up their excess electrons. That electrode is called the anode. In a similar manner, positively charged ions are attracted to the negative electrode where they can pick up electrons, and that electrode is called the cathode. The cathode is electron rich and the anode is electron poor. A reaction that loses electrons, where the species is oxidized and has its charge increased, is called the anodic reaction; and similarly a reaction where the species gains electrons and has its charge reduced is called the cathodic reaction.

All chemical reactions require some exchange of electrons. For any reaction to occur, a potential must force that exchange of electrons. The force that drives charged particles, electrons, is defined in volts. Thus volts drive all chemical reactions. The voltages that drive chemical reactions are evaluated on an arbitrary scale. Chemical reactions that occur in aqueous solutions can have their voltages established by comparison to an arbitrary standard, the voltage of the hydrogen gas / hydrogen ion equilibrium. This voltage is strongly dependent upon conditions so standard conditions are established. The standard conditions for hydrogen electrode are one atmospheric pressure of hydrogen gas in a solution of one molar hydrochloric acid on a platinized platinum electrode surface. This potential for this cell at these standard conditions is assigned the value of 0.00 volts.

For the measurement to have significance there must be equilibrium between hydrogen gas and hydrogen ion on solution. This requires a special surface on which hydrogen gas becomes water-soluble hydrogen atoms with very low inhibition. The surface determined to be most suitable for this application is platinized platinum. Platinization occurs when very finely divided platinum is plated on a polished surface of platinum metal. This produces a very high surface area that facilitates the disassociation and subsequent dissolution of hydrogen in water. A figure of the hydrogen electrode is seen below:

FIGURE 2.1 Standard hydrogen reference electrode. (3)

The standard condition for all other chemical cells is the pure substance in equilibrium with a one molar solution of its ions; or equilibrium mixtures of one molar ionic solutions with an inert spectator electrode. Frequently that electrode is either polished platinum or graphite. A chemical reaction is a combination of an oxidation process and a reduction process. Each of these processes is called half cell. The electrochemical potentials of half cells are determined by direct comparison to the potential of the hydrogen cell.

The role of the hydrogen electrode is to supply a constant known voltage, but difficulties with the mechanical construction of this electrode causes it to be used only sparingly. The same role can be accomplished using other standard cells. The fundamental principle necessary to be a standard cell is that the concentrations of the ions with respect to the metal components must be unchanging during the range of conditions in which the measurements are taken. Two of the most common standard cells are the

standard calomel cell (SCE) $\text{Hg}/\text{Hg}_2\text{Cl}_2$, and the silver silver chloride cell Ag/AgCl cell. Both of these cells are held to constant voltages because of the insolubility of salts in contact with the metals. In the calomel cell, calomel, mercurous chloride and mercury, are in contact with a saturated solution of potassium chloride. In the silver silver chloride electrode silver metal is contact with silver chloride and a saturated solution of potassium chloride. The potential of the calomel electrode is the oxidation potential of mercury to mercurous ion and for the silver silver chloride that potential is the oxidation potential of silver to silver ion. Both these potentials are regulated by the concentration of the ionic species. The low solubility product of the salts in the standard potassium chloride solution fixes this concentration so the potentials are constant. Figures of these electrodes are below:

FIGURE 2.2 Two designs for the calomel reference electrode: (a) laboratory construction ;(b) commercial construction.(4)

A measurement of the potential is accomplished by connecting the test half cell to the standard cell through a standard voltmeter. The test cell is typically the metallic species supported in a standard solution of ionic species. A wire connects the cells through a voltmeter. Since no current flow is possible without ion flow, an ionic flow path between the half cells must be established. This path is commonly called a salt bridge. Typically this is a simple glass U tube filled with one molar potassium chloride solution. Potassium chloride is used because the energy to cause potassium ions to flow is almost identical to the energy required to cause chloride ions to flow. Therefore there is no junction potential developed through the salt bridge. However, the salt bridge could also be a semi-porous membrane, or a porous frit between cells. The salt bridge prevents the mixing of the solution and still permits accurate potentials to be measured.

FIGURE 2.3 Salt Bridge

Because of the codependence of voltage and current an accurate half-cell voltage can not be determined when a current flows. The passage of current is due to the flow of ions. The charged ions layer the surface of the oppositely charged electrode. Therefore the bulk of the solution is screened from seeing the true charge of the electrode. This causes a polarization effect that corrupts the true potential measurement [polarization will

be discussed later in this thesis.] The polarization layers inhibit the free flow of ions. Since the oppositely charged ions filter the solution from seeing the true potential of the electrode and an artificial potential is seen. This can sometimes be reduced by rapidly rotating the electrode, which in effect is stirring the solution. The best procedure to get accurate voltage readings is to insert a large resistance between one of the electrodes and the voltmeter. This 'null' resistor reduces current flow to a minimum and thereby permits an accurate reading of the potential. A diagram of the system used to determine electrode potentials is in the Figure below.

FIGURE 2.4 Schematic cell showing a potentiometer and electrometer to measure Corrosion potential.(5)

Where M is a test electrode, N is a resistance and P is a potentiostat

In the figure above an electrometer with an internal resistance of about 10^{+14} Ohm is connected in series with a potentiometer. The potentiometer consists of a series of batteries equipped with a voltage divider. It is used to provide a constant potential between 0.1mv to 1.6 mv to the electrodes. The potential from potentiometer opposes the potential from the cells in the figure. The purpose is to balance the potential of the system so that no current flows and the potential can be read accurately on the electrometer. By this procedure, very accurate values for the potentials of half-cell reactions can be

determined. Tables have been prepared that list the potentials for chemical reactions.

Half-cells are commonly presented as reduction reactions. A typical listing of half-cell potentials is below:

TABLE 2.1 Standard Electromotive Force Potentials. (6)

<u>SHE)</u>	<u>Reaction</u>	<u>Standard Potential, E^0 (volts vs.</u>
Noble	$\text{Au}^{3+} + 3\text{e}^- = \text{Au}$	+1.498
	$\text{Cl}_2 + 2\text{e}^- = 2\text{Cl}^-$	+1.358
	$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- = 2\text{H}_2\text{O}(\text{pH } 0)$	+1.229
	$\text{Pt}^{2+} + 3\text{e}^- = \text{Pt}$	+1.118
	$\text{NO}_3^- + 4\text{H}^+ + 3\text{e}^- = \text{NO} + 2\text{H}_2\text{O}$	+0.957
	$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- + 4\text{OH}^- (\text{pH } 7)_a$	+0.82
	$\text{Ag}^+ + \text{e}^- = \text{Ag}$	+0.799
	$\text{Hg}_2^{2+} + 2\text{e}^- = 2\text{Hg}$	+0.799
	$\text{Fe}^{3+} + \text{e}^- = \text{Fe}^{2+}$	+0.771
	$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- = 4\text{OH}^- (\text{pH } 14)$	+0.401
	$\text{Cu}^{2+} + 2\text{e}^- = \text{Cu}$	+0.342
	$\text{Sn}^{4+} + 2\text{e}^- = \text{Sn}^{2+}$	+0.15
	$2\text{H}^+ + 2\text{e}^- = \text{H}_2$	0.000
	$\text{Pb}^{2+} + 2\text{e}^- = \text{Pb}$	-0.126
	$\text{Sn}^{2+} + 2\text{e}^- = \text{Sn}$	-0.136
	$\text{Ni}^{2+} + 2\text{e}^- = \text{Ni}$	-0.250
	$\text{Co}^{2+} + 2\text{e}^- = \text{Co}$	-0.277
	$\text{Cd}^{2+} + 2\text{e}^- = \text{Cd}$	-0.403
	$2\text{H}_2\text{O} + 2\text{e}^- = \text{H}_2 + 2\text{OH}^- (\text{pH } 7)_a$	-0.413
	$\text{Fe}^{2+} + 2\text{e}^- = \text{Fe}$	-0.447
	$\text{Cr}^{3+} + 3\text{e}^- = \text{Cr}$	-0.0744
	$\text{Zn}^{2+} + 2\text{e}^- = \text{Zn}$	-0.762
	$2\text{H}_2\text{O} + 2\text{e}^- = \text{H}_2 + 2\text{OH}^- (\text{pH } 14)$	-0.828
	$\text{Al}^{3+} + 3\text{e}^- = \text{Al}$	-0.1662
	$\text{Mg}^{2+} + 2\text{e}^- = \text{Mg}$	-2.372
	$\text{Na}^+ + \text{e}^- = \text{Na}$	-2.71
	$\text{K}^+ + \text{e}^- = \text{K}$	-2.931

2.1.2 Thermodynamic Considerations:

The electrical chemical potential is directly related to standard thermodynamic parameters by the equation below:

$$\Delta G = -n F \Delta E \quad (2.1.2.1)$$

ΔG is the Gibbs free energy; n is the number of electrons exchanged in the half reaction; F is Faraday's constant that represents the change of charge with the passage of one mole of electrons; and E is the electrode potential.

An illustration of the application of this equation can be accomplished by considering the following general reaction:

The free energy change from the standard states and the nonstandard free energy are expressed in the following equations:

$$\Delta G^0 = (c\Delta G^0 + d\Delta G^0) - (a\Delta G^0 + b\Delta G^0) \quad (2.1.2.4)$$

This equation is for the standard free energies. For the non-standard free energies the equation is written below:

$$\Delta G = (c\Delta G + d\Delta G) - (a\Delta G + b\Delta G) \quad (2.1.2.5)$$

The difference between the standard and non-standard free energies is in the equation below:

$$\Delta G - \Delta G^0 = [c(\Delta G - \Delta G^0) + d(\Delta G - \Delta G^0)] - [a(\Delta G - \Delta G^0) + b(\Delta G - \Delta G^0)] \quad (2.1.2.6)$$

By substituting chemical potentials in the above equations we get the equation below:

$$\Delta G = -nF [\Delta E_{\text{products}} - \Delta E_{\text{reactants}}] . \quad (2.1.2.7)$$

In the reaction above A is oxidized to A^+ and B^+ is reduced to B. Chemical potentials are listed as reduction potentials.. Since B^+ is being reduced to B in this reaction, the potential for the B^+ reduction can be taken from the tables. The half- cell for $A \longrightarrow A^+$ is the an oxidation half-cell potential, but the table gives a reduction potential. This reduction potential can be converted to an oxidation reaction by multiplication by -1. When the half-cells potentials of both half-cells of the reaction are algebraically added and if the sum is positive; when multiplied by $-nF$ the sign becomes negative. ΔG is negative so the reaction will go as written. If the sum is negative; when multiplied by $-nF$, ΔG will become positive and the reactions will not go as written, but will go in the reverse direction. If the sum is 0, then $\Delta G = 0$ and the system is in equilibrium.

It is important to realize that the chemical potentials for the half reactions are strongly dependent upon the concentrations of the species in the equation. This can be shown in the following development. By considering only one component in the reaction above, A; ΔG can be related to the concentrations by the following equation:

$$G - G^0 = RT \ln [A]^a \quad (2.1.2.8)$$

Where R is the gas constant; T is the temperature in degrees Kelvin; [A] is the concentration of A in moles/liter; a is the coefficient before A in the reaction.

The following equation can be used to represent the reaction above:

$$\Delta G - \Delta G^0 = RT \ln [B][A^+]/[A][B^+] \quad (2.1.2.9)$$

$$K = [B][A^+]/[A][B^+] \quad (2.1.2.10)$$

In the reaction described above all the reactants have coefficients of 1 so there are no exponents to which the concentrations have to be raised. The species labeled A and B are pure metals and are assigned a activity of 1 so the equation reduces to:

$$K = [A+]/[B+] \quad (2.1.2.11)$$

The development can be further advance by incorporating the equation relating the Gibbs free energy to electrochemical potential.

$$\Delta G = - nF\Delta E \quad (2.1.2.12)$$

By substituting this relation into the equation above we get the following equation:

$$\Delta E = \Delta E^0 - [RT/nF] [\ln K] \quad (2.1.2.13)$$

This is the Nernst equation. It shows how changing the concentration of the components of a reaction can change the potential of a cell. It is one of the most important relationships in electrochemistry.

By plotting the voltages of reactions against concentrations as expressed in the Nernst equation the relationship an be visualized. These plots are commonly called EH concentrations plots. When the systems are used to define corrosion reactions of metallic specie they are commonly called Pourbaix Diagrams.

2.1.3 Corrosion and Electrical Potential Diagrams:

Perhaps the most influential scientist to develop the theory of corrosion was Marcel Pourbaix. He published a series of lectures. One of the most useful concepts in this series of lectures was the development of electrochemical potential and concentration diagrams based on the Nernst equation. Since the potential of several corrosion reactions are dependent upon hydrogen ion concentration, these diagrams are frequently represented as electrochemical potential; pH plots. The diagrams can be used to define

the electrochemical conditions responsible for corrosion as a function of pH in water. In these plots the ordinate is pH and the abscissa is electrochemical potential.

All corrosion reactions take place in water so they are bounded by the oxidation and reduction of water. Thus the Pourbaix Diagrams all the systems are all defined within the boundaries of water decomposition. Therefore it is very important to establish these boundaries. Those reactions and their relationships to pH are considered below.

This is first reaction as written in acidic solution. In basic solution the equivalent

(Remember $K_w = 10^{-14} = [\text{OH}^-] [\text{H}^+]$ so the concentration of OH^- can be expressed as concentration H^+).

The potential of both reactions is a function of H^+ and can be written using the Nernst equation as seen below.

$$E = E_0 - (RT/nF) \ln [\text{H}_2]/[\text{H}^+]^2 \quad (2.1.3.3)$$

Pourbaix simplified this equation by substituting the values for R and F with $T = 298^\circ\text{K}$ and converting $\ln$ to $\log$. Since the $[\text{H}_2]$ is considered to have unit activity and n, the number of electrons exchange, the previous equation becomes:

$$E = E_0 + 0.059 \log [\text{H}^+] \quad (2.1.3.4)$$

This transposed to:

$$E = E_0 - 0.059 \text{ pH} \quad (2.1.3.5)$$

This represents the boundary equation for the reduction of hydrogen in water. Similarly the reduction of oxygen is in the reaction below:

The Nernst equation for the condition defined above is:

$$E = E_0 - 0.059\text{pH} \quad (2.1.3.8)$$

These equations represent the boundary for the reduction of oxygen in water.

The development continues when the standard potentials are substituted in to the respective equations. The E_0 for the reduction of hydrogen ion to hydrogen gas in acidic solution ($\text{pH} = 0$) is 0.00V and in base solution ($\text{pH}=14$) is -0.85 v. The E_0 for the reduction of oxygen in acidic solution is 1.22 v at $\text{pH} = 14$ that potential is 0.401v.

If we plot electrochemical potential against pH we have two lines dividing the plot into three zones. The zone above the top line defines the conditions where the oxidation of oxide to form oxygen to take place. Below the bottom line designating the zone where hydrogen ion is reduced to hydrogen gas. The zone between the lines represents the conditions where water is stable. See figure below:

FIGURE 2.5 Potential/pH diagram showing conditions of stability for water and its decomposition products, oxygen and hydrogen.(7)

All the chemical process in which metallic materials are corroded occurs within these boundaries.

Pourbaix simplified the chemical reactions responsible for the oxidation of metallic species in to three general equations. These three generic reactions are listed below:

The potentials as a function of the ion concentrations and pH of these three reactions can be incorporated into the Nernst as seen below:

$$E = E_0 - (0.059/n) \log[M^{+n}] \quad (2.1.3.12)$$

$$E = E_0 - 0.059 \log [M(OH)_n] + 0.059pH \quad (2.1.3.13)$$

$$E = E_0 + 0.059 \log [A]^a/[B]^b - m/n(0.059) pH \quad (2.1.3.14)$$

In the first of the Nernst equations above there is no pH dependence so on the Pourbaux Diagram reactions of this type these will be represented as horizontal lines. The next two equations have pH dependencies so they will be represented as sloping lines. The slope of the line is the coefficient of pH in the Nernst equation.

Pourbaix Diagrams are frequently plotted using two concentrations: 1 molar and 10^{-6} molar. Thus traditionally there are two lines for every reaction on the Pourbaix Diagram. The lines differ only in the initial E_0 which is a function of the initial ion concentration. Thus the first equation for the first chemical reaction written above would be plotted as two lines. The first line would represent the potential for the oxidation of the

metallic species from the metal in a one molar solution. The second line would represent the metallic species in one ppm (part per million or 1mg/l) concentration.

In addition to the oxidation reduction reactions that can be defined by the Nernst equation, other equations in which the metallic species is effected by pH must also be included in Pourbaix Diagrams. Typically these are precipitation and solubility reactions that are controlled by the pH and solubility products. These are used to account for the concentrations of various metallic ionic species as a function of pH on the Pourbaix Diagrams. Since they have no electrochemical potentials they appear as vertical lines on the Diagrams. These equations can be generalized as below:

$$\mathbf{K = [M(OH)_a] [H+]^a/[M^{+a}]} \quad (2.1.3.16)$$

$$\mathbf{K = K_{sp}} \quad (2.1.3.17)$$

$$\mathbf{pK = \log [M^{+a}] + a \, pH} \quad (2.1.3.18)$$

$$\mathbf{pH = pK/a - \log [M^{+a}]/a} \quad (2.1.3.19)$$

Because the research in this thesis is limited to the corrosion of iron, only the Pourbaix Daigram for iron will be developed. The equations representing the oxidation of iron are given below. Below each oxidation reaction is the accompanying Nernst equation used to draw the Pourbiaux Diagram. The reactions are written from the most reduced Fe to most oxidized Fe⁺³ Included within the oxidation reduction reactions are the solubility equations. These can easily be differentiated in the list of equations because the redox equations all start with E values and the solubility equations all start with pH. The values in the redox equations are the standard electrochemical potentials using one

molar solution. On the Diagram there will be two parallel lines: one for the standard potential and the other for the ppm ion concentration.

$$E_{\text{Fe/Fe}^{+2}} = -.440 + 0.0295\log[\text{Fe}^{+2}]$$

$$E_{\text{Fe/Fe}(\text{OH})_2} = -0.470 - 0.059\text{pH}$$

$$E_{\text{Fe/HFeO}_2^-} = 0.495 - 0.886\text{pH} + 0.295\log [\text{HFeO}_2^-]$$

$$\text{pH} = 6.65 - 0.5\log[\text{Fe}^{+2}]$$

$$\text{pH} = 14.30 + \log [\text{HFeO}_2^-]$$

$$E_{\text{Fe}^{+2}/\text{Fe}(\text{OH})_3} = 1.057 - 0.1773\text{pH} - 0.059 \log [\text{Fe}^{+2}]$$

$$\text{pH} = 1.613 - 1/3(\log[\text{Fe}^{+3}])$$

$$E_{\text{HFeO}_2^-/\text{Fe}(\text{OH})_3} = -0.810 - 0.059 \log[\text{HFeO}_2^-]$$

$$E_{\text{Fe}(\text{OH})_2/\text{Fe}(\text{OH})_3} = 0.271 - 0.0591\text{pH}$$

The previous nine equations (8) are used to describe the iron system. In equations where electrons are exchanged the equations are followed by the appropriate potential

relationships. In equations where the solubility of the species occurs, the equations are followed by values that show the solubility relationship with respect to pH. When these equations are plotted the following Pourbaix Diagram is produced.

FIGURE 2.6 Pourbaix diagram for iron.(9)&(34)

Corrosion only occurs when soluble materials are produced so the Pourbaix Diagram can be used to define the corrosion domain by shading in those areas. This is seen in the figure below:

FIGURE 2.7 Pourbaix diagrams for iron. All dissolved species activities of 10^{-6} g-equiv/L.(10)

2.2 Current Flow and the Rate of Corrosion

As discussed earlier the electrochemical potential is a thermodynamic function so it can be used to predict whether or not a reaction will occur. If a reaction can occur it is important to be able to predict how fast that reaction can occur. The reaction rate is dependent upon current flow. For iron, in the figure above, if the electrical potential and pH of the solution fall within the zone of passivation, then corrosion will not occur; but if it falls outside that zone, where a reaction will occur, and there will be corrosion. If the rate of the reaction can be so slow that effectively the reaction isn't occurring, then the effects of corrosion will not be felt.

Since corrosion reactions involve a flow of electrons, the rate of reaction is proportional to the current flow. This was clearly demonstrated by Faraday and is shown in Faraday's law shown below:

$$w = Ikt \quad (2.2.1)$$

w is the weight of materials corroded or plated

k is a constant that equals the atomic weight of the element being corroded divided by number of electrons exchanged in the reaction multiplied by

Faraday's constant that equals the charge transported by one mole of electrons.

I is the current flow in amps

t is time in seconds.

An understanding of processes that control the flow of electrons during the corrosion process is necessary to appreciate the rate of corrosion.

2.2.1 Current Density:

Consider the following situation two pieces of copper immersed in water in separate system. One piece of copper is 10 square millimeters and the other is only one square millimeter. They both corrode. It is easy to conclude that the larger piece corrodes 10X faster the smaller piece. This is because there is 10 times the exposed surface in the large piece. Current is passed as a multiple of surface area. This is the concept of current density.

2.2.2 Exchange Current:

The experiment above may seem unexpected because there is only one metal immersed in the solution. There is no obvious anode and cathode; yet the copper will corrode. This is because the sample of metal is not a single crystal. Metallic samples are usually poly-crystalline solids and every crystal has defects that make it unique from the other crystals in the specimen. Different numbers and types of defects cause the crystals to be at different energy states. Some of the crystals are electro-positive with respect to adjacent crystals. If a conducting solution connects two crystals, the potential difference between the two crystals can drive a current; and therefore force a corrosion process. One crystal is the anode and the other is the cathode. The anode forces electrons to the cathode and becomes ionized and dissolves. [This is the fundamental process in rusting of iron.]

Let us consider the activation process necessary to form ions from a metallic crystal immersed in a solution. The metal atoms must release its electrons to the base metal crystal. The newly formed ion still retains an attraction for those electrons. Until the solution energy, due to the hydration of the ion by the solvent, over comes the energy of attraction of the ion to its electrons, the ion remains on the surface of the electrode. As

soon as the solution energy is more negative than the electron attraction energy, the ion migrates from the electron surface. In this process the metallic atom donates its electron to the metal and becomes a cation. By imposing a potential on the electrode the ability of the metal atom to loose electrons can be affected and this affects the energy barrier between atoms and ions.

There is a free energy difference between the base metal and the cations, in the case being discussed, copper and copper ions. Since the reaction goes from $\text{Cu} \rightarrow \text{Cu}^{+2}$, the energy state of the product ions is much lower than the initial energy state of the reacting metal. But before the copper can ionize and react to form ions, it must overcome an energy barrier. The energy of the atoms of the base metal must overcome the activation energy before they become ions in the solution. (See the figure below).

FIGURE 2.8 An energy profile for copper in pure water: $i_a > i_c$.(11)

By that figure it is easy to see that it will be harder for the ion species to overcome the energy barrier and plate out as the metal, than it will be for the metal to form ions.

The ordinate is free energy. Since free energy is equal to:

$$\Delta G = -nF\Delta E \quad (2.2.2)$$

by changing ΔE , imposing a potential on the electrode, the free energy of the metal can be reduced and that its respective ion is increased.

The barrier energy difference between metal and its ion is reduced. Where the energies of the species approach each other, the rate of the backward reaction increases and the rate of the forward reaction decreases. A particular state occurs when the rate of the forward reaction equals the rate of the reverse reaction. This is illustrated in the figure below.

FIGURE 2.9 An energy profile for copper in equilibrium with a solution of its divalent ions: $i_a = -i_c = i_v$. (12)

This means that the current density for the forward reaction equals the current density of the reverse reaction. There is current flowing but the current flowing of the forward reaction equals the current flow of the reverse reaction. The current at this equilibrium condition is called the exchange current density, and is represented as i_0 .

2.3 Activation

When a voltage is impressed on a system of two electrodes immersed in a solution. This can be done if the half cells of two metallic systems are attached with a conducting wire. One electrode becomes electron rich and the other electrode becomes electron poor. The electron rich cell is called the cathode and the electron poor electrode is the anode. Ions in the solution migrate to the surface of the electrodes where they either give up electrons or gain electrons in order to reduce the potential impressed on the electrodes. [This only occurs if a current flow between the electrodes through the wire.]

Consider the situation of an electrode immersed in water. In this case, let that electrode be a piece of iron. The area near the surface of electrode can be divided into three zones: the bases metal, the electrolyte solution solid interface, and the electrolyte solution. When the iron sample is first immersed in the water, the first event that occurs is the passage of metal ions into the electrolyte side of the liquid solid interface. The process of formation of ions requires the ions remain associated with the metal side of the interface and the electrons they have left behind. Thus we can imagine the metal as a negatively charged solid surrounded by a coating of cations.

2.3.1 Double layer effect:

When the solution energy is more negative than the energy of attraction of the cation and the electrons on the metal surface, the ions will migrate into the solution. The difference in the energy is commonly over potential or activation polarization. The migration process is based on the solution ion attraction energy. The concentration of ion in the vicinity of the electrode is not uniform. The nonhomogenous distribution of ions in the electrolyte is commonly referred to as the double layer.

The double layer consists of two parts:

- a) A compact layer, the Helmholtz layer, closest to the electrode surface in which the distribution of charge varies linearly with distance from the electrode surface
- b) The second layer is more diffuse. It is commonly referred to as the Gouy Chapman layer in which the charge varies exponentially with distance.

This can be seen in the figure below:

FIGURE 2.10 The double layer: (a) Distribution of ions as a function of an electrode behaving as an anode. (b) Variation of potential with distance for the model in (a).(13)

Eventually the double layer effect will come to steady state. Whenever the equilibrium is perturbed, a new dynamic equilibrium is established. There is a continuous flow of anions and cations in the electrolyte, adjacent to the electrode surface that performs the current carrying requirements of the electrode reactions. The corrosion potential of a metal may be considered the negative charge developed on it when it is placed in an electrolyte. When corrosion occurs the electrons produced by the anodic

metal are conducted away to the cathode. The negative potential of the metal is reduced and the corrosion potential is reduced.

2.3.2 Activation current density:

Consider two different metals Zn and Fe. Both have negative standard potentials (see table 2.1). If both were separately placed in water both would acquire negative charges, they would reduce their negativity by forming positive ions and corroding. If they were attached through a wire, the potential for pushing electrons through a circuit is greater for Zn; so Zn would push its electron through the wire to Fe and reduce the negative charge on the Zn. This would be accompanied by ionization and formation of Zn^{+2} . The electrons pushed to Fe increase its negativity which is not reduced by ionizing so it does not produce cation and corrode. [This is the fundamental principle in the anti corrosion technique called sacrificial anodic potential].

The current flow parameter of ions that are produced on a base metallic surface can be directly related to thermodynamic parameters. The rate of corrosion can be defined by the following equation:

$$v = k_{\text{corr}} [\text{reactants}] \quad (2.3.2.1)$$

Where k_{corr} is the rate constant for the corrosion process and $[\text{reactants}]$ is equal to the concentration of the reactants. We know from the Boltzmann relationship that:

$$k = A \exp (-\Delta G^*/RT) \quad (2.3.2.2)$$

Where ΔG^* is the activation energy

By combining the above equations we get:

$$v = A \exp (-\Delta G^*/RT) [\text{reactants}] \quad (2.3.2.3)$$

We measure velocity of corrosion reactions by current flow. At equilibrium:

$$i_a = i_c = i_o = A_o \exp (-\Delta G^*/RT) \quad (2.3.2.4)$$

When the forward reaction is faster than the reverse reaction equilibrium is destroyed and the free energies of the metal and its ions are at different levels just as seen in the figure 2.8. This deviation from the equilibrium potential is a combination of both the anodic polarization on the base metal and the cathodic polarization on the ions species. When an external potential is applied to the cathode, the energy of the metal has increased and the energy of the ionic species has decreased. The change in energy of the base metal and its respective ions as a result of the applied potential is called polarization energy. The figure below shows this effect:

FIGURE 2.11 An energy profile for an anode at equilibrium, represented by the curve M_o/M_o^{z+} and a similar profile for an anodic activation polarization of, represented by the curve M_a/M_a^{z+} .(14)

The total polarization effect is designated as η . The polarization, η , is the potential change $E - e$, from the equilibrium half cell potential, caused by a net surface

reaction rate for the half cell reaction. In cathodic polarization, η_c , electrons are supplied to the electrode surface and build up in the metal due to the slow reaction rate causes the surface potential, E , to be negative with respect to e . Therefore η_c is negative. In anodic polarization electrons are removed from the electrode surface. The resulting efficiency causes a positive charge on the anode so η_a must be positive. It is important to remember that η is in the unit of volts, and it is the difference from the standard half -cell potential.

The difference between the energy state of the metal and the ions is $\alpha\eta nF$ and is referred to as anodic polarization. The coefficient α indicates anodic polarization. Similarly cathodic polarization is energy difference between the equilibrium energy state for the metal ion and the non equilibrium metallic ion. The energy state coefficient for cathodic polarization is $(1-\alpha)$. The polarization, expressed in volts, has been converted to free energies by multiplying by nF . This enables us to determine the new activation energy for the anodic reaction which can be seen as $(\Delta G^* - \alpha\eta nF)$ because the energy state of the metal is increased and the activation energy is reduced. The anodic current can be expressed in the equation below:

$$i_a = A_o \exp [(-\Delta G^* + \alpha\eta nF)/RT] \quad (2.3.2.5)$$

This can be simplified as below:

$$i_a = A_o \exp (\Delta G^* /RT) * \exp (\alpha\eta nF/RT) \quad (2.3.2.6)$$

Now we know:

$$i_o = A_o \exp (-\Delta G^*/RT) \quad (2.3.2.7)$$

By substitution

$$i_a = i_o \exp (\alpha\eta nF/RT) \quad (2.3.2.8)$$

$$\ln i_a = \ln i_o + \alpha\eta nF/RT \quad (2.3.2.9)$$

Now let:

$$\alpha n F / RT = A^* \quad (2.3.2.10)$$

The equation becomes:

$$\ln (i_a/i_o) = A^* \eta \quad (2.3.2.11)$$

Convert this to log base 10 and the result is:

$$\eta = [2.303/A^*] \log (i_a/i_o) \quad (2.3.2.12)$$

Now let:

$$\beta = 2.303 RT / \alpha n F \quad (2.3.2.13)$$

The equation above can be written in the form below:

$$\eta = C \ln i + D \quad (2.3.2.14)$$

Where $C = 2.303/A$ and $D = 2.303/A(\ln i_o)$

This is known as the Taffel equation.

For the anodic reaction the following equation can be used to describe it:

$$\eta_a = \beta_a \log i_a - \beta_a \log i_o \quad (2.3.2.15)$$

and the cathode equation is just below:

$$\eta_c = \beta_c \log i_c - \beta_c \log i_o \quad (2.3.2.16)$$

$$\beta_a = 2.303 RT / \alpha n F \quad (2.3.2.17)$$

$$\beta_c = 2.303 RT / (1-\alpha) n F \quad (2.3.2.18)$$

This is the standard equation seen in many reference texts:

$$i_a = i_o e^{E/B} \quad (2.3.2.19)$$

Where E is the half-cell potential and B is the Taffel slope. As described above there is another equation that is identical for the cathodic reaction that equation is:

$$i_c = i_o e^{E/B} \quad (2.3.2.20)$$

The overall reaction is the sum of the anodic and cathodic contribution. This is represented in the equation below:

$$B_a \ln i_a/i_o + B_c \ln (i_c/i_o) = E_a - E_c \quad (2.3.2.21)$$

[This equation will be used to establish the equilibrium conditions for the chemical system studied in this thesis.]

The constants β_a and β_c are the anodic and cathodic Tafel slopes. Examination of the Tafel equation shows that a plot of η against $\ln i$ for both the anodic and cathodic processes should be linear. The slope of that line should be β_a and β_c respectively. The intercept D which is equal to $\beta \ln i_o$ enables the direct determination of i_o in a given electrolyte.

It is obvious that the conductivity of the solution is directly related to the ion concentration in the electrolyte. Different electrolytes will have different Tafel slopes and different equilibrium exchange currents. When current is measured it is the difference between the anodic current flow and the cathodic current flow. This is seen in the following equation:

$$i_{\text{meas}} = i_a - i_c \quad (2.3.2.22)$$

If the anodic parameters are to be measured the following equation applies:

$$\eta_a = \beta_a \log [(i_{\text{meas}} + i_c)/i_o] \quad (2.3.2.23)$$

Obviously when $i_{\text{meas}} \gg i_c$ linear behavior will be observed. However at polarization close to E_{corr} i_a is comparable to the true value of i_o the measured value of current will be removed from the true value of i_a and the linearity will be lost. This is illustrated in the following figures. The value for the exchange current will be best approximated by extrapolations of the linear portions of the plot.

FIGURE 2.12 Two Tafel plots: a) Theoretical Tafel plot. B) An idealized practical Tafel plot. (15)

Tables of exchange currents and Tafel slopes for various half reactions in electrolytic solution have been prepared. [The table below is an example of such a table.]

TABLE 2.2 Electrode Kinetic Parameters, 20_25C°. (16)

Electrode	Solution	i_0 (A/cm ²)	β_c (V)	β_a (V)	Reference
Reaction:	$2H^+ + 2e^- \rightarrow H_2$				
Pt	1 N HCl	10^{-2}	0.03		11
	0.1 N NaOH	0.7×10^{-3}	0.11		11
Pd	0.6 N HCl	2×10^{-3}	0.03		11
Mo	1 N HCl	10^{-5}	0.04		11
Au	1 N HCl	10^{-5}	0.05		11
Ta	1 N HCl	10^{-4}	0.08		11
W	5 N HCl	10^{-4}	0.11		11
Ag	0.1 N HCl	5×10^{-6}	0.09		11
Ni	0.1 N HCl	8×10^{-6}	0.31		11
	0.12 N NaOH	4×10^{-6}	0.10		11
Bi	1 N HCl	10^{-6}	0.10		11
Nb	1 N HCl	10^{-6}	0.10		11
Fe	1 N HCl	10^{-5}	0.15		11
	0.52 N H ₂ SO ₄	2×10^{-5}	0.11		12
	4% NaCl, pH 1-4	10^{-6}	0.10		8
Cu	0.1 N HCl	2×10^{-6}	0.12		11
	0.15 N NaOH	10^{-5}	0.12		11
Sb	2 N H ₂ SO ₄	10^{-8}	0.10		11
Al	2 N H ₂ SO ₄	10^{-9}	0.10		11
Be	1 N HCl	10^{-8}	0.12		11
Sn	1 N HCl	10^{-7}	0.15		11
Cd	1 N HCl	10^{-6}	0.20		11
Zn	1 N H ₂ SO ₄	2×10^{-10}	0.12		11
Hg	0.1 N HCl	7×10^{-12}	0.12		11
	0.1 N H ₂ SO ₄	2×10^{-12}	0.12		11
	0.1 N NaOH	3×10^{-14}	0.10		11
Pb	0.01-8 N HCl	2×10^{-12}	0.12		11

TABLE 2.2 (CONT.)

Electrode	Solution	i_0 (A/cm ²)	β_c (V)	β_a (V)	Reference
Reaction: Pt	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ 0.1 N H ₂ SO ₄	9×10^{-11}	0.10		11
Reaction: Pt	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ 0.1 N NaOH	4×10^{-12}	0.05		11
	Au 0.1 N NaOH		5×10^{-12}	0.05	11
Reaction: Pt	$Cl_2 + 2e^- \rightarrow 2Cl^-$ 1 N HCl	5×10^{-3}	0.11	0.13	11
Reaction: Fe	$M \rightarrow M^{n+} + ne^-$ 0.52 N H ₂ SO ₄	10^{-7}		0.060	12
	0.52 N H ₂ SO ₄	10^{-10}		0.039	12
	0.63 N FeSO ₄	3×10^{-9}		0.060	13
				0.075	
	4% NaCl, pH 1.5			0.068	9
	0.3 N H ₂ SO ₄			0.10	14
	0.5 M FeSO ₄ ,	3×10^{-10}		0.030	15
	0.1 M NaHSO ₄				
	Perchlorate			0.030	16
Cu	0.001 N Cu(NO ₃) ₂	10^{-9}			11

Please note that the Taffel slope for the cathodic reaction of hydrogen on iron reactions is very similar in all solutions in the table 2.2, and the exchange current is also nearly constant. The anodic reaction of iron also has a nearly constant Taffel slope but the exchange current is quite dependent upon the electrolytic condition of the solution.

2.4 Measurement of Current and Polarization Effects

The three electrode cell is the standard laboratory apparatus for the quantitative investigation of corrosion phenomena. The system can be seen in the figure below:

FIGURE 2.13 The three electrode cell. (17)

The three electrodes are: (1) the standard reference electrode, (2) the working electrode and (3) the auxiliary electrode. The standard electrode provides a constant potential reference against which the other measurements are made using the other electrode. The working electrode is a special electrode which houses the test sample. The auxiliary electrode will be used to impose variable potential on the working electrode.

(1) The Working Electrode:

The working electrode is the name given to the electrode being investigated. It is desirable to have the exposed surface of that electrode be 100 square millimeters so current measurements can be conveniently converted to current densities. Both anodic and cathodic measurements can be made on this electrode by applying the external potential in both directions sequentially. Commonly samples of the specimen being studied are mounted in a plastic resin and so only the desired surface is exposed. The

surface of the metal is polished to eliminate any imperfections and produce more accurate measurements. An example of commercial electrode available for metallic systems is seen in the following figure:

FIGURE 2.14 Designs for working electrodes: a) cylindrical specimens. b) Disc specimens.(18)

(2)The Auxiliary Electrode:

The auxiliary electrode is simply used to carry current in the circuit created by the investigation. It is only important that it is non-reactive in the system. It is not used to make potentials measurements. Commonly, a piece of graphite is used; in special cases a platinum wire is used.

(3)The Reference Electrode:

The reference electrode is used to provide a stable data point against which the potential of the working electrode can be measured. It can not carry any more than the

most negligible current. In most situations the reference electrode is the standard calomel cell (SCE).

The circuit consists of three components:

a) A current measuring device: this could be capable of reading milliamps or preferably microamps.

b) A potential measuring device: it is important that no current be drawn when the potential is measured. A traditional potentiometer, similar to that used the half cell potential measurement, can be used for this purpose.

c) A potential source to drive the working electrode such that the desired cell reactions occur. A simple constant voltage source is not able to maintain this balance. A potentiostat is commonly used for this purpose. Potentiostats supply a predetermined potential to the working electrode so that measurements of the cell current can be made. This is done by alternating the current at the counter electrode to whatever value is necessary to maintain the set potential value between the working and the reference.

In a typical experiment, the electrolyte concentration plays a very important role. The electrolyte carries the current. For the standard reference electrode to provide an accurate reference voltage the conductance path of the electrolyte must be as short as possible. If that path is too long, then ohmic potential drop due to ionic migration through the solution, will effect the potential difference between the working and reference electrode. A unique salt bridge that minimizes the ion conducting path is used in these systems. This device reduces the internal ohmic potential drop to a minimal value. This is called the Luggin capillary. Traditionally a Luggin Capillary is a glass tube with a very

small capillary tip just adjacent to the working electrode surface. It is usually filled with saturated potassium chloride, a standard electrolyte for salt bridges see the figure below:

FIGURE 2.15 Simple capillary made from glass tube salt bridge. (19)

Measurements of applied potential and current density are taken using the three electrode system described above. Typically both positive and negative current values are obtained. When all the current values are plotted as positive values, a figure below like that for the copper system will be seen:

FIGURE 2.16 Potentiodynamic scan for copper in 3.5 percent sodium chloride solution. (20)

In this figure the portion of the graph that had negative currents is from -400 mv to -240 mv. This represents the reactions in which copper was behaving as an anode. The portion of the plot in which the currents were positive was from -240 mv and above. This represents the reactions in which copper is behaving as a cathode. The voltage at which this change over occurs is commonly called the corrosion potential and is represented with the following symbol, E_{corr} . At this potential the system could be considered in a pseudo equilibrium state, equivalent to that which would occur when the potentiostat is switched off. True equilibrium conditions are impossible to obtain because metallic systems are assemblages of micro crystalline environments. Each different crystal has its own potential. The difference in the different crystal potentials forces corrosion to occur. Therefore the corrosion potential at this condition represents only a pseudo state.

It should be recognized that the plot above was not linear as was anticipated from the previous derivations (see equation 2.3.2.20). This is usually to any one or combinations of the following situations:

- (1) There is more than one electrode reaction occurring .
- (2) The scan rate was too fast.
- (3) The conductivity of ions in the solution was diffusion controlled. This last case deserves special consideration.

2.5 Concentration Polarization

As in all kinetic systems the only reaction seen is the slowest step. In section 2.3 an understanding of activation polarization was developed. The previous discussions developed in this section had focused on the activation steps of electrochemical reactions. In these steps the ions are formed and then disassociate or associate with the electrons

and either migrate to the solution or plate out on the electrode surface. The migration of ions both into and out the bulk solution also plays an important role. These effects are commonly called concentration polarization. When current is passed to the solution by the electrons from the metallic surface in a cathodic reaction, ions must migrate from the solution to the surface of the electrode. The ions of like charge repel each other so although the ionic density at the electrode surface is not very high it is much higher than the bulk of the solution. Generally there is a crowding of ions at the surface. This inhibits more ions from receiving electrons from the electrode surface. The simple existence of a potential results in a demand for more current flow. This causes a layering of ions at the surface which causes concentration gradient reflected as a difference on the concentration of ions with respect to the distance from the surface. This effect can be seen in the figure below:

FIGURE 2.17 The variation of anion concentration with distance from a cathode. (21)

A simple model to understand this phenomenon can be developed from Fick's First Law of diffusion.

$$\mathbf{J} = -\mathbf{D}(\mathbf{dc/dx}) \quad (2.5.1)$$

Where **J** is the flux of the substance

D is the diffusion coefficient

dc/dx is the concentration gradient.

Faraday's Law of Electrolytes states that

$$\mathbf{i} = \mathbf{nFJ} \quad (2.5.2)$$

This can better be represented as

$$\mathbf{i} = -\mathbf{nFD}(\mathbf{dc/dx}) \quad (2.5.3)$$

If we assume the concentration gradient is linear as in the figure above this equation can be reduced as follows.

$$\mathbf{I} = -\mathbf{nDF} (\mathbf{c}_0 - \mathbf{c})/\mathbf{x} \quad (2.5.4)$$

c_0 is the concentration of ions in the bulk of the solution. The negative sign only indicates that current is being carried away from the cathode. Since we are only interested in the magnitude of the current and it is greatest when $c = 0$. [Notice that when $c > c_0$ the concentration of ions in the region of the electrode is increasing and the current would be flowing in the opposite direction. The sign would be reversed.] The equation above can be further reduced as follows.

$$\mathbf{I} = -\mathbf{nDF} (\mathbf{c}_0/\mathbf{x}) \quad (2.5.5)$$

At the condition when no current flow the potential of the system can be expressed in the Nernst equation as follows.

$$\mathbf{E}_1 = \mathbf{E}_0 + \mathbf{0.059/n} \log [\mathbf{c}_0] \quad (2.5.6)$$

For condition 2 when current does flow the Nernst equation is described below

$$\mathbf{E}_2 = \mathbf{E}_0 + \mathbf{0.059/n} \log [\mathbf{c}] \quad (2.5.7)$$

Previously it was shown that the polarization η is the difference between the potential states due to the polarization at the electrode surface. This would be given by the equation below

$$\eta = 0.059/n [\log (c)/(c_o)] \quad (2.5.8)$$

$$c/c_o = (1 - i/i_{\text{meas}})$$

This results in the following equation

$$\eta = 0.059/n \log (1 - i/i_{\text{meas}}) \quad (2.5.9)$$

As $i \rightarrow i_{\text{meas}}$ then $\eta \rightarrow \infty$ The overall effect of diffusion on the polarization is easy to discern. For small currents where $i_{\text{meas}} \rightarrow 0$ because $i_c \rightarrow i_o$ the linearity of the E vs. $\log i$ will not be obtained. For intermediate currents where $i_{\text{meas}} \rightarrow i_c$ the equation will produce linear sections. It is because of this that solutions with significant electrolyte concentrations are used in these measurements. When solutions with low electrolyte concentrations are used unreliable data are obtained.

An appreciation of the relationship described above can be obtained by plotting the potential the exchange current, the current density, and Taffel slope for both the cathodic and anodic half -cell on the same graph.

FIGURE 2.18 The Daniell cell. The individual free corrosion potentials of the copper[©] and zinc (a) are changed to a cell potential, $E_{\text{corr}(\text{cell})}$, when the metals are short circuited. The limiting current density, I_L , is never achieved because of the finite internal resistance of the cell.(22)

In the research under taken by the study, very dilute electrolyte solutions are used. Because of this the traditional methods used to evaluate corrosion can not be applied. However the principles discussed in the above section are still valid and need to be understood to appreciate this research. Certain concept developed above will be used in the analyses of data collected, so a familiarity with those terms is important.

2.6 Mixed Potential Theory

With good experimental data, one can predict the corrosion potential, E_{corr} , and the corrosion current, i_{corr} of the system. This is done using fundamental principles of Mixed Potential Theory. In this situation plots of the log of the current density against the

potential are linear for both the cathodic and anodic representations of metallic reactions. The graphical representations are called Evan's Diagrams (20). They are prepared by plotting the potential the exchange current, the current density, and Taffel slope for both the cathodic and anodic half cell on the same graph. The slope of the lines will be the Taffel slopes of each of the half reaction. Cathodic half reactions will have positive slopes and anodic half reactions will have negative slopes.

FIGURE 2.19 Theoretical Tafel plot.(23)

A reaction between the two half reactions can be represented as the sum equations for the cathodic half reaction and the anodic half reaction. This situation is defined in the following equation:

$$B_a \ln i_a/i_o + B_c \ln (i_c/i_o) = E_a - E_c \quad (2.6.1)$$

This will become clear by using the following example. Consider two species A and C. The standard potential or corrosion potential of A is much more negative than C.

When C and A are connected, A will be oxidized and C will be reduced. The half reactions are as follows.

Given that the corrosion potential of both species is known, the Tafel slope of each process is known and the exchange current for each reaction is known the following plot can be drawn.

FIGURE 2.20 The Daniell cell. The individual free corrosion potentials of the copper and zinc (a) are changed to a cell potential, $E_{\text{corr}(\text{cell})}$, when the metals are short circuited. The limiting current density, i_L , is never achieved because of the finite internal resistance of the cell.(24)

The point of intersection of the anodic half reaction line and the cathodic half reaction line is the critical point. The value on the abscissa is the current density i_{corr} for corrosion. The value of the intersection point of the ordinate is the corrosion potential for the reaction. E_{corr} .

The Evan's Diagram can also be constructed by reversal of this process. When the equilibrium has been reached, the weight of metallic species oxidized can be used to calculate the current. This can be converted to current density by division of the current by the surface area. That equals the current density of corrosion, i_{corr} . The solution potential at equilibrium conditions can be measured using inert electrodes as compared to a standard reference electrode. The electrochemical potential of the half cell reaction can be taken from tables or measured using inert electrodes as described earlier. Since the Taffel slope for most reactions are nearly identical, they can be taken from tables. The exchange current densities, particularly for the anodic metallic half cell are the least consist values and seem to vary with electrolyte conditions most dramatically. By using Taffel slope from the tables, the exchange current density can be calculated and the Evan's Diagram constructed. From the Evans Diagram the corrosion rate, based on corrosion current density as a function of change the electrochemical potential of the half- cell reaction, can be determined.

2.7 The Focus of this research

In this study the oxidation of iron is to be eliminated or reduced by enriching the solution with hydrogen gas at atmospheric pressure. An Evan's Diagram for the oxidation of a metal in an acid solution can be constructed (SEE Figure below):

FIGURE 2.21 A metal, M , corroding in an acid solution with the evolution of hydrogen. The microstructure of the metal causes it to act as its own anode and cathode; the cathode reaction is the reduction of hydrogen ions.(25)

In this construct notice that the potential of the hydrogen cell is 0.00 volts. This is the condition for 1 atm of H₂ gas bubbled over a Platinum electrode in a 1 molar hydrochloric acid solution. Distilled water has a pH of 7; this would significantly reduce that potential. The voltage of the aqueous hydrogen half cell can be reduced by infusion of hydrogen gas which would result in greater dissolution of hydrogen in water. If that effect in combination with a low hydrogen ion concentration reduces the H₂/H⁺ half cell potential to less the oxidation potential of iron, then corrosion will be impossible. The

corrosion potential of ion is less than the standard potential because in the ion corroding system the concentration of ion is one ppm. The corrosion potential for iron is taken from the Pourbaix diagram and is -0.62 v. To eliminate the corrosion of iron the potential of the H_2/H^+ half cell would have to be more negative than -0.62.

If by infusion of hydrogen gas in water the potential can be reduced, but not to a more negative value than the oxidation potential of iron; then corrosion will continue. By lowering the H_2/H^+ half cell potential, the rate of that corrosion can be significantly reduced. The point of intersection of the lines on the Evans Diagram will occur at lower current densities. If the reduced corrosion rate of the pipe can be compensated by the flow rate of water such that concentration of less than 1 ppm Fe^{+2} are produced, then iron pollution has been effectively arrested.

Because the solution used in this experiment is distilled water the conductivity is extremely low. Analysis of the electrochemical parameters described in some detail above will not be possible, the use of electrolyte enriched solutions will not be a true representation of the phenomena occurring in the actual system. Therefore it was decided that the effect of hydrogen addition of hydrogen to the water on the corrosion of iron would be measured directly and then parameters described above would be back calculated.

2.8 Corrosion Control:

There are two methods to prevent or reduce corrosion:

2.8.1 Coating:

Protect the material from the corroding by isolating it from the environment. The application of a surface coating usually does this. If the oxidizing environment can be

insulated from the potentially corroding material then no reaction can occur. In most common systems metallic materials are painted. The paint is an impenetrable barrier through which the oxygen or oxidizing species cannot penetrate. No reaction is possible.

2.8.2 Electric potential:

Change the chemical potential of the system so it is positive. When the chemical potential on the system is positive, then Gibbs free energy is also positive; and it is thermodynamically impossible for the system to corrode. Electrochemical potential of metallic system can be made more positive by two different ways:

a) Anodic Protection:

In the first procedure, a more electronegative metal (a metal whose electrochemical potential is more negative than the base metal) is directly attached to the metal to be protected. As it is shown in the following figure:

FIGURE 2.22 Cathodic protection with a sacrificial anode. (26)

In such a system the more active metal is sacrificed to protect the base metal. That is the more electronegative metal will be oxidized thereby sacrificing itself and protecting the base metal. Electrons from the more active metal are passed to the base metal. When this is done the more active metal is oxidized. Metallic ions are produced. This more active metal is called the anode, (electrons go from the anode to the cathode). The protected metal is called the cathode. Positive ions in the solution travel to the cathode. As the more active metal loses electrons and becomes ionized the less active metal receives these electrons and the positive ions in the solution pick up these electrons and are reduced to their lower valence state as a result of the flow current. Since this is a reduction the less active metal can not be oxidized and is therefore protected.

The most important feature of this protection approach is that both electrodes must be in the same electrochemical environment and that environment must be conductive. If they are not in the same environment then an ionic current flow is impossible and no protection will be afforded. Just the fact that the electrodes are directly attached is of little consequence. They must be in a continuous 'aqueous union' because the circuit is completed by ion flow. The ion flow is only possible when the electrodes are in the same solution.

(b) Cathodic Protection:

In the second procedure an inert metal is attached through a potential source to the metal to be protected. As it is shown in the following figure:

Figure 2.23 Cathodic protection by impressed current. (27)

The potential source provides electrons to the protected metal in a manner similar to the sacrificial anode system. Positive ions in solution travel to the electron rich, protected metal. An inert metal is attached to the opposite pole of the potential source. This site is electron poor and acts as the anode. If the anions are oxidized then current flows and the cations are reduced at the protected surface; if not, then the simple polarization of the surfaces protects the base metal. The degree of reaction is measured by current flow. This latter procedure is used to protect automobiles from corrosion. The positive terminal of the battery is attached to the driving motor while the negative terminal is attached to the body of the auto. At rest the body of the car is negatively charged. Hydrogen ions will accept the electrons from the body and thus protect the car. Again the ground anode and protected cathode must be in the same environment and the environment must be conductive. The circuit is completed by ion flow. If the electrodes are in a non conductive environment the base metal will not be protected.

2.9 The Hypothesis of this Proposal

The goal of this research is to prevent the corrosion of the iron pipes used to transport water to the citizenry of the Arabian Peninsula. The dissolved ferrous ion in the water is further oxidized to ferric oxide and colors the water red. It also affects the taste of the water. In the background section of this proposal we have shown that iron to ferrous even at concentrations as low as 10^{-3} mg/l has an oxidation potential of -0.62v . This potential is below the reduction potential of hydrogen ion to hydrogen gas. It is then expected that thermodynamically the oxidation of iron will proceed in solutions that are mildly acidic or neutral. It has also been shown that the rate of the current flow of this oxidation reaction for solutions with moderated conductivity is high enough to cause the water to be polluted. There are two options that are to be explored in this research:

(1) Stop the reaction:

If the electrochemical potential of the H_2/H^+ half cell could be decreased below the oxidation potential for Fe/Fe^{+2} cell then corrosion of iron would be impossible. This might be possible if appreciable quantities of hydrogen gas can be solubilized in water. The solubility of hydrogen gas is effected by pressure and temperature. At higher pressures more hydrogen dissolves. But it would be ideal if enough hydrogen could be dissolved at atmospheric pressure. Experimental measurements of the corrosion of steel material simulating the pipe materials will be made in hydrogen enriched solution to test this option.

(2) Decrease the rate of the reaction so corrosion has no consequence:

The second method to control corrosion involves decreasing the current flow so the water flow will compensate for any iron dissolved and thereby reduce the concentration to tolerable levels.

In the background section of this thesis we have shown the relationship of current and corrosion potential. This was based on accepted Taffel slope and exchange current density values from standard tables. By examination of the Evans' Diagram, it is shown how iron current flow is effective in establishing the corrosion rate of iron. [This is the current at the intersection current for the reduction reaction of hydrogen and the oxidation current for the oxidation of iron.] By dissolving more hydrogen in the water the reduction potential of hydrogen ion to hydrogen gas can be made more negative. This would drop the line for the hydrogen reduction step in the Figure 2.21. The current flow at the intersection of the reduction of hydrogen and the oxidation of iron would move towards lower current density. This would reduce the rate of iron oxidation and if the potential and corresponding current flow were reduced to a value such that the flow of water through the pipe would compensate for the corrosion rate then the iron levels in the water would be low enough as to be "non polluting". To determine how low the corrosion current density can be decreased. The Evans Diagram will be developed as explained earlier.

CHAPTER 3

Experimental

Prelude

The techniques used to measure the controlling parameters are typically done in conducting solutions. Distilled water is not a conductor solution so use of the three electrode system will not provide accurate measurements. For our system, it would be more useful to determine the rate of corrosion and back calculate the controlling parameters. The corrosion rate of simulate pipe steel coupons will be evaluated in distilled water into which various amounts of hydrogen gas will be dissolved. The hydrogen and hydrogen- nitrogen gas mixture will be provided by a gas cylinder and bubbled through the water at a controlled flow rate at specific time period. The resulting solution will have various solution potentials. The solution potentials will be adjusted by increasing the amount of dissolved hydrogen. The potential of the solution will be measured by external potentiostat equipped with platinum electrodes. The corrosion rate will be determined by measuring the amount of iron that oxidized as a function of time. From this, the current flow can be calculated. By knowing the corrosion current and surface area the current density can be calculated. The time at which the system is in pseudo equilibrium will be determined. The current density at this time is the corrosion current density. The corrosion potential of the solution at the equilibrium conditions will be measured. The corrosion current density and corrosion potential is the point of intersection of the anodic half reaction and cathodic half reaction lines on the Evan's Diagram. The Taffel slope will be taken from the tables. By knowing the Taffel slope, the corrosion current and corrosion potential, the exchange current density for the anodic and

cathodic half reaction can be calculated. From the Evan's Diagrams the effect of changing potential needed to eliminate or reduce the rate of oxidation to acceptable level can be determined. Finally, by using the Nernst equation the pressure of hydrogen required to dissolve the needed amount to reduce the potential of the hydrogen reduction cell to tolerable limits can be determined.

3.1 Experimental procedure

In this portion of the thesis the exact experimental procedure used to prepare and analyze the sample is presented. This section is divided into sections that are specific to different aspects to the experimental procedure.

3.1.1 The Metal Samples:

The exact specifications of the steel used to make the water conduit pipes in Saudi Arabia were unavailable so it was decided to use a low carbon, plane carbon steel for this test. This is a general, less specific, material, and any results that were obtained from these materials can be directly applied to the steel materials used in the pipe manufacture. A sheet of rolled 1017 steel was purchased from McMaster Carr. The sheet was 18" by 12" and was 1/16 inch thick. It was sheared in to squares of 1" by 1" dimensions. It is understood that through this shearing process it is not possible to obtain identical dimensions for each square. The surface of the squares had already been corroded so each square was polished on the grinding table using a fine alumina grinding compound. Both flat faces of each square were polished. Each face was so smooth that by visual inspection the scratch lines were erased. The polished coupons were stored in a glass vessel under a nitrogen blanket to inhibit further corrosion until use. In total there were 80 coupons. Each coupon was weighted and the weight error

was determined. These assessments established the range of sizes since the coupons all have the same thickness.

3.1.2 The Plastic Bags:

Each coupon is to be placed in a plastic bag containing a test solution. The test solution is water that is partially saturated with a mixture of hydrogen and nitrogen gas. The bag contains the test solution and coupon is sealed and placed into a second plastic bag. The atmosphere in the second bag is matched to the blend of gases bubbled into the water of the test solution. The second bag is sealed and resealed. By this procedure an external atmosphere nearly identical to that used to saturate into the second bag. The water will enclose the test samples. This should prevent diffusion of the gases from the water.

The atmospheric control could only be insured with the proper gauge plastic bags. Although metallic coated bags to store hydrogen containing gas mixture can be purchased, the metallic coating would create a sacrificial anode system with the aqueous solution so these were not chosen. Instead a heavy gauge polyethylene bag was chosen. Bags of this type were purchased from McMaster Carr. Both the water containing bag and the atmospheric bag were equipped with “zip-loc” seals. These were used to close the bags as they were moved from the hood where the gas infusion took place. After the bags were removed from that environment, they were heat sealed using a ‘Seal-a- Meal’ bag sealed. This was purchased from Southern States.

3.1.3 The Gas Infusion System:

As described above the water was infused with a blend of nitrogen and hydrogen gases. Two cylinders: one of hydrogen and one of nitrogen, were purchased from West

Virginia Welding Supply. Each cylinder was equipped with a pressure regulator and a rotometer. The flow volume on the rotometer ranged from 1 Standard Cubic Foot per Min(SCFM) to 8 SCFM. The flow was adjusted to 2 SCFH. Between the flow meter and the solution was an appropriated length of Tygon tubing so the infusion could be done in the hood. An “air stone” terminated the Tygon tubing. This insured good dispersion of the gases as they flowed through the water. The gases were permitted to flow for specified time periods. This is detailed in the data section of this thesis. After the gases infused for the specific time the flows were turned off. The electro chemical potential of the solution was measured using a potentiostat.

3.1.4 The Measurement of the Solution Potential

One of the most important aspects of this study was the establishment of the electrochemical potential of the solution. This was done using the potentiostat, two platinum electrodes, a reference cell and a small container that was divided into two chambers. The platinum electrodes were cylindrical metal screen type; they were immersed in the aqueous solution. The potentiostat measures the potential difference in the test cell and subtracts it from the potential difference in the control cell. It records the difference in these potentials. The system is shown in the following figure:

FIGURE 3.1 The system photograph

The solution preparation system was a two chambered three electrode system. Two of the electrodes were in the test chamber. One of these electrodes was a platinum electrode the other was a silver/silver chloride reference cell. The reference cell (Ag/AgCL) was prepared as per the directions of the manufacturer. The second chamber of the system was a sample of pure water which connected to the test chamber by a membrane. The membrane served the same purpose as a salt bridge. In the second chamber was the other platinum electrode. It should be noted that both platinum electrodes were identical as they are shown below:

FIGURE 3.2 The three electrodes system

3.1.5 Sample preparation details:

The volume of the infusion system was 2.5 gallons. Each sample required 500 mls of solution and each suite contains 8 samples. Therefore, the volume of test solution for all the samples of a suite could be prepared at one time. The samples were prepared by bubbling the appropriate mixture of hydrogen and nitrogen into the water contained the

large volume chamber of the preparation cell for designated time. The solution potential was measured using potentiostat. Although the values fluctuated in the 10^{-3} mv range the largest absolute value was used. At least two runs of gas infusion were made to insure that the same voltage was produced by identical treatment. Five hundred milliliter aliquots of the solution were decanted from the preparation cell into each bag of the suite. A weighted metal coupon had already been placed in the bag. The bags were closed with the “zip-log” mechanism and later thermally melt sealed.

The sealed bags, contain the sample coupon, and test solution were placed in a larger bags. The same gas mixture used in the solution preparation was flushed into the larger surrounding the smaller test bag. This insured that the atmosphere surrounding the test solution bag was identical to that used to prepare the test solution. The second enclosing bag was closed using zip log mechanism and the thermally sealed. The double bags samples were permitted to sit on the laboratory bench until they were opened at the designated time.

3.1.6 Primarily experiments:

Several primarily experiments were done to insure accuracy of the process. Before any electrochemical potential measurements were used, the cell was tested against a 1 molar ferric sulfate solution. The voltage agreed with the theoretical voltage. This validated the process for making electrochemical potential measurements. Further it was anticipated that the preparation of the samples required a significant amount of time would pass so it was decide to measure the rate of change of the electrochemical potential for that time period. A sample of water was saturated with hydrogen and the potential was followed for 15 minutes. During that time the potential only changed about 2

hundredth volts. This insured that the solution was stable during the bagging and sample preparation. It is also important to note that pH measurement was not made with the hydrogen saturated solutions because the glass electrode becomes erratic in the presence of soluble hydrogen.

3.1.7 The Sampling Procedure:

After the samples were prepared as described above, they were permitted to sit on the laboratory bench. Every two days they were turned over. A large stirring table is unavailable so the samples remained in a static position. Since all the samples were identical, it was felt that the identical treatment would not affect the corrosion rate results. At specific time intervals, every 2 days, samples were opened for testing. First the atmospheric bag was cut to remove the sealed sample bag. Then the sealed sample bag was cut. The sample solution was poured into a 1000 ml Erlenmeyer flask. The sample bags were shaken before decanting the liquid to suspend any iron oxides that might have collected the bottom of the bag. Iron staining of the bag where the steel coupon rested was observed. This was dissolved in a few milliliters of aqueous solution of 50% phosphoric acid. The solution was poured into the flask. The metal coupon also has some rust sites. These were also dissolved in a few mls of the phosphoric mixture. This solution was also added to the flask. The solution in the flask was heated. As the temperature increased more of the iron oxide dissolved. Twenty five milliliters nondiluted phosphoric acid was added to dissolve any non-soluble iron oxide. After all the iron species dissolved, the solution was clear and colorless. It was permitted to cool to room temperature and decanted into a 1000 ml volumetric flask. The solution was diluted

to the 1000 ml mark with pure water. The sample was shaken to insure complete mixing and a sample for iron analysis was removed. The remaining sample was discarded.

3.1.8 The Analysis of Iron in Solution:

The samples collected using the above-mentioned procedure were analyzed using atomic absorption spectroscopy. A Beer's Law plot was prepared using standard iron solutions. Absorption measurements of the iron solution were taken and concentrations of iron in the part per million range were determined by comparison to the Beer's Law plot. If any sample's absorption did not fall within the region of linearity of the Beer's law plot, that sample was diluted to insure the validity of its concentration.

3.2 Data collected

There are several types of data collected during the process of this experimentation:

- (1) Solution potential data of the H_2/H^+ half-cell: This was done using the potentiostat and platinum electrodes compared to a silver silver chloride electrode.
- (2) Saturating atmospheric data: This includes flow rate and gas composition for specified times. These flowing gas systems were used to change the potential of the cell and change the rate of corrosion of the iron
- (3) Surface area of the samples: These data included the measurement of the bulk surface area. The plates were polished to remove any large grooves that would enhance the rate of corrosion.
- (4) Weight of iron corroded: These data were calculated from the atomic absorption analyses of the solution.

(5) Time: The time in these experiments was measured in days. Because the reaction is so slow, the days are the appropriate time interval. The samples were opened during the same hours of the day, so the time is consistent

3.3 Data analysis Method

3.3.1 Weight of Iron that Corroded:

The concentration of iron which reacted as a result of the corrosion reactions was determined by Atomic Absorption Spectroscopy. This result is obtained by comparing the absorption values of the test samples to absorption values for known standards.

Concentration is linear with absorption for a set of known concentrations so by linear comparisons the concentrations of the unknown sample solutions can be determined. The unit of the concentrations is parts per million (ppm). The samples had to be diluted so their absorption would fit into this linear range. Accurate results required that the collected data be corrected for that dilution, then the weight of iron corroded will be extracted by converting from ppm to gram. That procedure is explained in the following two steps:

a) Correction for dilution factor:

The original solution was 500 milliliters. The iron solution produced by corrosion was solubilized using a solution of 50% phosphoric acid, and diluted to 1000 milliliters. This is a dilution factor of 2. In order to have the atomic absorption analyze the solution in the linear range of the standard samples ten milliliters of the solution were further diluted to 100 hundred milliliters. This is dilution factor of 10. The total result is a dilution factor of 20. Therefore all concentration values have to be multiplied by 20 to get the true concentration.

b) Conversion of measured values to grams:

The concentration in results are reported in the number of ppm multiplied by 10^{-3} to yield grams and then multiplied by 20 to correct for the dilution factor as it is shown in the following equation:

$$W(\text{gm}) = 10^{-3} * \text{ppm} * 20(\text{L}) \quad (3.3.1.1)$$

3.3.2 The current flow determination:

The current needed to produce the quantity of iron solubilized by the corrosion reaction is determined by the Faraday's Law:

$$w = kIt \quad (3.3.2.1)$$

w equals the weight of the metal solubilized in grams.

k equals the atomic weight of the metal/ (number of electrons exchanged * faraday's constant).

I equal the current flow in Amperes.

t is the time in seconds.

Given the weight of iron dissolves from step one above the current flow can be directly calculated.

3.3.3 Calculation of the current density:

The current density is simply the current divided by the surface area. The surface area is directly measured. The current density for each sample in the various suites can be determined by the following equation:

$$i_d = I/SA \quad (3.3.3.1)$$

Where I is the current flow and SA is the surface area.

3.3.4 The Establishment of the Equilibrium Corrosion Rate Condition:

Before any conclusions can be reached reaction equilibrium has to be established. The time for that establishment must be determined. From the earlier discussion it is known that the current density is related to the exchange current through the Taffel slope and cell potential as in the following equation.

$$i_d = i_o e^{E/B} \quad (3.3.4.1)$$

Where:

i_d = current density

i_o = exchange current

E = cell potential

B = Taffel slope

In the system being studied the Taffel slope and exchange current are constant. An equation can be written for the anodic reaction and the cathodic reaction. The overall reaction is the sum of both these reactions. The weight of the iron dissolved can be used to determine the time at which the reaction stabilized by application of the following equation:

$$w = k \cdot SA \cdot t \cdot i_o \cdot e^{(E_a - E_c)/(B_a - B_c)} \quad (3.3.4.2)$$

This equation can be linearized by converting the equation above to its logarithmic form as is shown below:

$$\ln w = (E_a - E_c)/(B_a - B_c) [\ln k + \ln SA + \ln t] + (E_a - E_c)/(B_a - B_c) i_o \quad (3.3.4.3)$$

If the logarithm of the weight of iron dissolved is plotted against the logarithm of the time a straight line should result. The corrosion potential represented by $(E_c - E_a)$ and the Taffel slopes represented by $(B_a - B_c)$ are constant. It is understood that when the

reaction starts, $E_a - E_c$ is not a constant value, equilibrium has not been reached. When the preequilibrium data are plotted a steep slope will be produced. The changes to the system will result if rapid changes. After equilibrium has been reached the rate of change with respect to time will be constant and linear and the slope will not be steep. The slope of the line will be $(E_a - E_c)/(B_a - B_c)$. Plots of the logarithm of the weight of iron dissolved are plotted against the logarithm of time in seconds.

CHAPTER 4

RESULTS & DATA ANALYSIS

4.1 Correlation Factor

Since the AA results have no unit, AA measurements follow the Beer's Law in which the absorption is linear with concentration; five standard samples were analyzed by AA to get correlation factor for the data as it is shown in the following table and figure:

TABLE 4.1 Values of iron concentration measuring by AAU for standard samples

Iron concentration (ppm)	AAU Reading
0.00	0
1.00	0.05
2.00	0.086
3.00	0.136
4.00	0.170
5.00	0.206

FIGURE 4.1 Beer's Law plot

From this figure the linear equation is:

$$Y(\text{Iron conc in AAU reading}) = 0.041 * X(\text{PPM}) + 0.0051$$

$$X = (Y - 0.0051) / 0.041$$

4.2 Results

The AA is used to measure iron concentration in each sample. By using previous correlation factor the iron concentration are presented in ppm unit. The following tables show variation of iron concentration with time at different conditions.

TALBE 4.2 Variation of iron concentration with time (H₂/N₂ (3 CF/min)& 5 min&E_{cell}= -0.433v)

Unite	gm	Day		ppm
sample#	Weight	Test time	AAU Reading	[Iron]
1	7.5	2	0.023	0.4365
2	7.42	4	0.095	2.192
3	7.55	6	0.117	2.72
4	7.5	8	0.149	3.509
5	7.47	10	0.167	3.948
6	7.84	12	0.189	4.485
7	7.46	14	0.209	4.973
8	7.43	16	0.227	5.412

TABLE 4.3 Variation of iron concentration with time (N₂(3 CF/min)& 10 min & E_{cell}=0.345v)

Unite	gm	Day		ppm
sample#	Weight	test time	AAU Reading	[Iron]
9	7.758	2	0.038	0.8024
10	7.376	4	0.097	2.241
11	7.370	6	0.135	3.168
12	7.4037	8	0.156	3.6804
13	7.454	10	0.183	4.339
14	7.476	12	0.202	4.802
15	7.48	14	0.218	5.192
16	7.48	16	0.238	5.68

TABLE 4.4 Variation of iron concentration with time(H₂/N₂ &10 min&E_{cell}=-0.556v)

Unite	gm	day		ppm
sample#	Weight	test time	AAU Reading	[Iron]
17	7.41	2	0.021	0.387
18	7.45	4	0.087	1.997
19	7.51	6	0.115	2.68
20	7.54	8	0.146	3.436
21	7.49	10	0.158	3.729
22	7.46	12	0.185	4.387
23	7.43	14	0.198	4.704
24	7.46	16	0.212	5.046

TABLE 4.5 Variation of iron concentration with tim(H₂/N₂& 20mint& E_{cell}=-0.565v)

Unite	gm	day		ppm
sample#	Weight	test time	AAU Reading	[Iron]
25	7.57	2	0.020	0.363
26	7.46	4	0.080	1.826
27	7.46	6	0.087	1.997
28	7.83	8	0.141	3.3146
29	7.53	10	0.151	3.558
30	7.54	12	0.178	4.217
31	7.48	14	0.194	4.607
32	7.47	16	0.201	4.778

TABLE 4.6 Variation of iron concentration with time (H₂ &10 min&E_{cell}= -0.585v)

Unite	gm	day		ppm
sample#	Weight	test time	AAU Reading	[Iron]
33	7.46	2	0.019	0.339
34	7.45	4	0.079	1.802
35	7.49	6	0.110	2.55
36	7.44	8	0.137	3.217
37	7.82	10	0.157	3.704
38	7.79	12	0.184	4.3641
39	7.55	14	0.197	4.680
40	7.75	16	0.205	4.875

TABLE 4.7 Variation of iron concentration with time (H₂& 20 mint &E_{cell}=-0.597v)

Unite	gm	day		ppm
sample#	Weight	test time	AAU Reading	[Iron]
41	7.45	2	0.015	0.241
42	7.43	4	0.062	1.387
43	7.53	6	0.099	2.290
44	7.45	8	0.128	2.997
45	7.73	10	0.138	3.241
46	7.84	12	0.151	3.558
47	7.68	14	0.167	3.948
48	7.67	16	0.198	4.704

TABLE 4.8 Variation of iron concentration with time(2H₂/N₂(6 CF of H₂/3 CF of N₂)/min For 20 min & E_{cell} = -0.59v)

Unite	gm	day		ppm
sample#	Weight	test time	AAU Reading	[Iron]
49	7.40	2	0.020	0.363
50	7.39	4	0.047	1.0219
51	7.39	6	0.063	1.412
52	7.61	8	0.106	2.46
53	7.53	10	0.123	2.875
54	7.81	12	0.135	3.168
55	7.43	14	0.158	3.729
56	7.41	16	0.167	3.948

TABLE 4.9 Variation of iron concentration with time (2H₂/N₂(6 CF of H₂/3 CF of N₂)/min For 10 min & E_{cell} = -0.557v)

Unite	gm	day		ppm
sample#	Weight	test time	AAU Reading	[Iron]
57	7.48	2	0.031	0.631
58	7.44	4	0.075	1.704
59	7.61	6	0.095	2.192
60	7.49	8	0.098	2.265
61	7.56	10	0.103	2.387
62	7.55	12	0.138	3.241
63	7.46	14	0.152	3.5829
64	7.42	16	0.192	4.558

TABLE 4.10 Variation of iron concentration with time(Co2 &10min & $E_{\text{cell}} = 0.433 \text{ v}$)

Unite	gm	day		ppm
sample#	Weight	test time	AAU Reading	[Iron]
65	7.77	2	0.05	1.905
66	7.42	4	0.12	2.80
67	7.53	6	0.132	3.095
68	7.66	8	0.154	3.631
69	7.80	10	0.178	4.217
70	7.77	12	0.190	4.5097
71	7.40	14	0.195	4.631
72	7.51	16	0.215	5.119

From the previous tables the variation of iron concentration with time for all experiments can be summarized in the following table:

TABLE 4.11 Variation of iron concentration with time at different conditions

infusion gas	Exp#	Ecell volt	Iron concentration (ppm)							
			2 days	4 days	6 days	8 days	10 days	12 days	14 days	16 days
CO2 10 min	9	0.412	1.905	2.80	3.095	3.631	4.217	4.5097	4.631	5.119
N2 10 min	2	0.345	0.8024	0.8024	3.168	3.6804	4.339	4.802	5.192	5.68
H2/N2 5 min	1	-0.433	0.4365	2.192	2.72	3.509	3.948	4.485	4.973	5.412
H2/N2 10 min	3	-0.556	0.387	1.997	2.68	3.436	3.729	4.387	4.704	5.046
2H2/N2 10 min	8	-0.557	0.631	1.704	2.192	2.265	2.387	3.241	3.5829	4.558
H2/N2 20 min	4	-0.565	0.363	1.826	1.997	3.3146	3.558	4.217	4.607	4.778
H2 10 min	5	-0.585	0.339	1.802	2.55	3.217	3.704	4.3641	4.680	4.875
2H2/N2 20 min	7	-0.59	0.363	1.0219	1.412	2.46	2.875	3.168	3.729	3.948
H2 20 min	6	-0.597	0.241	1.387	2.290	2.997	3.241	3.558	3.948	4.704

4.3 Comparison of the corrosion rate as a function of hydrogen dissolved

From the previous results, it is clear that iron concentration is affected by three factors:

1) The ratio mixture of bubbled gases 2) The infusion time 3) The type of bubbled gas.

The concentration of iron dissolved vs. time can be tabulated for each of the suites of samples. Since each suit of samples was prepared at different electrochemical potentials, direct comparison of these figures will show the effect of hydrogen dissolution on corrosion rate.

FIGURE 4.2 The variation of iron concentration with time at constant H2 /N2 flow rate (3 CF/min)

FIGURE 4.3 The variation of iron concentration with time at constant H2 flow rate (3 CF/min)

FIGURE 4.4 The variation of iron concentration with time at different ratio mixture

FIGURE 4.5 The variation of iron concentration with time for different types of gases

4.4 Calculate the weight of the material converted in the reaction

From the pervious data the values of iron concentration (ppm) are known so the weight of the material converted in the reaction (w) could be determined by using the following equation:

$$W(\text{gm}) = 10^{-3} * \text{ppm} * 20(\text{L}) \quad (4.4.1)$$

Where w weight of Iron that Corroded (gram) and ppm is the iron concentration
The weight values are shown in the following tables in this section.

In addition, The equilibrium corrosion rate condition will be established by applying the following equation:

$$\ln w = (\text{Ea}-\text{Ec})/(\text{Ba}-\text{Bc}) [\ln k + \ln \text{SA} + \ln t] + (\text{Ea}-\text{Ec})/(\text{Ba}-\text{Bc}) i_o \quad (4.4.2)$$

$$y = mX + I$$

Where $y = \ln w$ and $x = \ln k + \ln \text{SA} + \ln t$

The values of K and SA are constant, their values are shown below:

$$k = M / n * F = 55.845(\text{g/mole}) / 2 * 96485(\text{c/mole}) = 0.0002893 \text{ g/c}$$

$$\ln k = \ln(0.0002893) = -8.148$$

$$\text{Also } \text{SA}(\text{Surface area}) = 2(1.1\text{m} * 1.1 \text{ cm}) + 2(1.1 \text{ cm} * 0.15\text{cm}) + 2(1.1 \text{ cm} * 0.15\text{cm})$$

$$\text{SA} = 3.08 \text{ cm}^2$$

$$\ln 3.08 = 1.1249$$

Now, the following tables show the weight of the material converted in the reaction and the figures confirm the equilibrium corrosion rate condition:

TABLE 4.12 The weight of the material converted in Experimental #1*

Unite	ppm	w(g)		s		lnk+ln SA + ln t
sample#	[Iron]	y	lnw	Test time	Int	X
1	0.4365	0.00873	-4.74099	172800	12.05989	5.036750135
2	2.192	0.04384	-3.12720	345600	12.753037	5.729897316
3	2.68	0.0536	-2.92620	518400	13.158502	6.135362424
4	3.4365	0.06873	-2.67756	691200	13.446185	6.423044496
5	3.948	0.07896	-2.53881	864000	13.669328	6.646188048
6	4.217	0.08434	-2.47289	1036800	13.85165	6.828509605
7	4.607	0.09214	-2.38444	1209600	14.0058	6.982660284
8	4.778	0.09556	-2.34800	1382400	14.139332	7.116191677

FIGURE 4.6.a variation of weight material converted with time for initial reaction in exp#1*

FIGURE 4.6.b variation of weight material converted with time starting with 4 days in exp#1*

* Experimental #1 conditions: H₂/N₂ bubbled in the distilled water for 5 mints at 3 SCFM

TABLE 4.13 The weight of the material converted in Experimental #2*

Unite	ppm	w(g)		s		lnk+ln SA + ln t
sample#	[Iron]	y	lnw	Test time	Int	X
9	0.8024	0.016048	-4.13217	172800	12.05989	5.036750135
10	2.241	0.04482	-3.10510	345600	12.753037	5.729897316
11	3.168	0.06336	-2.75892	518400	13.158502	6.135362424
12	3.6804	0.073608	-2.60900	691200	13.446185	6.423044496
13	4.339	0.08678	-2.44437	864000	13.669328	6.646188048
14	4.802	0.09604	-2.34299	1036800	13.85165	6.828509605
15	5.192	0.10384	-2.26490	1209600	14.0058	6.982660284
16	5.68	0.1136	-2.17507	1382400	14.139332	7.116191677

FIGURE 4.7.a variation of weight material converted with time for initial reaction in exp#2*

FIGURE 4.7.b variation of weight material converted with time starting with 4 days in exp#2*

* Experimental #2 conditions: N2 bubbled in the distilled water for 10 mints at 3 SCFM.

TABLE 4.14 The weight of the material converted in Experimental #3*

Unite	ppm	w(g)	lnw	s		lnk+ln SA + ln t
sample#	[Iron]		Y	Test time	Int	X
17	0.387	0.00774	-4.86135	172800	12.05989	5.036750135
18	1.997	0.03994	-3.22037	345600	12.75304	5.729897316
19	2.68	0.0536	-2.92620	518400	13.1585	6.135362424
20	3.436	0.06872	-2.67771	691200	13.44618	6.423044496
21	3.729	0.07458	-2.59588	864000	13.66933	6.646188048
22	4.387	0.08774	-2.43337	1036800	13.85165	6.828509605
23	4.704	0.09408	-2.36361	1209600	14.0058	6.982660284
24	5.046	0.10092	-2.29342	1382400	14.13933	7.116191677

FIGURE 4.8.a variation of weight material converted with time for initial reaction in exp#3*

FIGURE 4.8.b variation of weight material converted with time starting with 4 days in exp#3*

* Experimental #3 conditions: H₂/N₂ bubbled in the distilled water for 10 mints at 3 SCFM

TABLE 4.15 The weight of the material converted in Experimental #4*

Unite	ppm	w(g)	lnw	s		lnk+ln SA + ln t
sample#	[Iron]		Y	Test time	Int	X
25	0.363	0.00726	-4.925	172800	12.05989	5.0367
26	1.826	0.03652	-3.309	345600	12.75304	5.7298
27	1.997	0.03994	-3.220	518400	13.1585	6.1353
28	3.3146	0.066292	-2.713	691200	13.44618	6.4230
29	3.558	0.07116	-2.642	864000	13.66933	6.6461
30	4.217	0.08434	-2.472	1036800	13.85165	6.8285
31	4.607	0.09214	-2.384	1209600	14.0058	6.9826
32	4.778	0.09556	-2.348	1382400	14.13933	7.1161

FIGURE 4.9.a variation of weight material converted with time for initial reaction in exp#4*

FIGURE 4.9.b variation of weight material converted with time starting with 4 days in exp#4*

* Experimental #4 conditions: H₂/N₂ bubbled in the distilled water for 20 mints at 3 SCFM

TABLE 4.16 The weight of the material converted in Experimental #5*

Unite	ppm	w(g)	lnw	s		lnk+ln SA + ln t
sample#	[Iron]		Y	Test time	Int	X
33	0.399	0.0079	-4.83081	172800	12.05989	5.0367
34	1.802	0.0360	-3.32312	345600	12.75304	5.7298
35	2.55	0.051	-2.97593	518400	13.1585	6.1353
36	3.217	0.064	-2.74357	691200	13.44618	6.4230
37	3.704	0.074	-2.60261	864000	13.66933	6.6461
38	4.3641	0.087	-2.43861	1036800	13.85165	6.8285
39	4.68	0.093	-2.36872	1209600	14.0058	6.9826
40	4.875	0.097	-2.32790	1382400	14.13933	7.11619

FIGURE 4.10.a variation of weight material converted with time for initial reaction in exp#5*

FIGURE 4.10.b variation of weight material converted with time starting with 4 days in exp#5*

* Experimental #5conditions: H2 bubbled in the distilled water for 10 mints at 3 SCFM

TABLE 4.17 The weight of the material converted in Experimental #6*

Unite	ppm	w(g)	lnw	s		lnk+ln SA + ln t
sample#	[Iron]		Y	Test time	Int	X
41	0.241	0.00482	-5.334	172800	12.05989	5.0367
42	1.387	0.02774	-3.584	345600	12.75304	5.7298
43	2.29	0.0458	-3.083	518400	13.1585	6.1353
44	2.997	0.05994	-2.814	691200	13.44618	6.4230
45	3.241	0.06482	-2.736	864000	13.66933	6.6461
46	3.558	0.07116	-2.642	1036800	13.85165	6.8285
47	3.948	0.07896	-2.538	1209600	14.0058	6.9826
48	4.704	0.09408	-2.363	1382400	14.13933	7.1161

FIGURE 4.11.a variation of weight material converted with time for initial reaction in exp#6*

FIGURE 4.11.b variation of weight material converted with time starting with 4 days in exp#6*

* Experimental #6 conditions: H₂ bubbled in the distilled water for 20 mints at 3 SCFM

TABLE 4.18 The weight of the material converted in Experimental #7*

Unite	ppm	w(g)	lnw	s		lnk+ln SA + ln t
sample#	[Iron]		Y	Test time	Int	X
49	0.6317	0.0126	-4.37136	172800	12.05989	5.0367
50	1.0219	0.0204	-3.89035	345600	12.75304	5.7298
51	1.412	0.028	-3.56701	518400	13.1585	6.1353
52	2.46	0.0492	-3.01186	691200	13.44618	6.4230
53	2.875	0.0575	-2.85597	864000	13.66933	6.6461
54	3.168	0.063	-2.75892	1036800	13.85165	6.8285
55	3.729	0.0745	-2.59588	1209600	14.0058	6.9826
56	3.948	0.0789	-2.53881	1382400	14.13933	7.1161

FIGURE 4.12.a variation of weight material converted with time for initial reaction in exp#7*

FIGURE 4.12.b variation of weight material converted with time starting with 4 days in exp#7*

* Experimental #7 conditions: 2H₂/N₂ bubbled in the distilled water for 20 mints at 3 SCFM

TABLE 4.19 The weight of the material converted in Experimental # 8*

Unite	ppm	w(g)	lnw	s		lnk+ln SA + ln t
sample#	[Iron]		Y	Test time	Int	X
57	0.631	0.0126	-4.37247	172800	12.05989	5.0367
58	1.704	0.0340	-3.37904	345600	12.75304	5.7298
59	2.192	0.0438	-3.12720	518400	13.1585	6.1353
60	2.265	0.0453	-3.09444	691200	13.44618	6.4230
61	2.387	0.0477	-3.04198	864000	13.66933	6.6461
62	3.241	0.0648	-2.73614	1036800	13.85165	6.8285
63	3.582	0.0716	-2.63610	1209600	14.0058	6.9826
64	4.558	0.0911	-2.39513	1382400	14.13933	7.1161

FIGURE 4.13.a variation of weight material converted with time for initial reaction in exp#8*

FIGURE 4.13.b variation of weight material converted with time starting with 4 days in exp#8*

* Experimental #8conditions: 2H₂/N₂ bubbled in the distilled water for 10 mints at 3 SCFM

TABLE 4.20 The weight of the material converted in Experimental # 9*

Unite	ppm	w(g)	lnw	s		lnk+ln SA + ln t
sample#	[Iron]		Y	Test time	Int	X
73	1.905	0.0381	-3.26754	172800	12.05989	5.0367
74	2.8	0.056	-2.88240	345600	12.75304	5.7298
75	3.095	0.0619	-2.78223	518400	13.1585	6.1353
76	3.63	0.0726	-2.62279	691200	13.44618	6.4230
77	4.217	0.0843	-2.47289	864000	13.66933	6.6461
78	4.5097	0.0901	-2.40579	1036800	13.85165	6.8285
79	4.631	0.0926	-2.37925	1209600	14.0058	6.9826
80	5.119	0.1023	-2.27906	1382400	14.13933	7.1161

FIGURE 4.14.a variation of weight material converted with time for initial reaction in exp#9*

FIGURE 4.14.b variation of weight material converted with time starting with 4 days in exp#9*

* Experimental #9conditions: CO₂ bubbled in the distilled water for 10 mints at 3 SCFM

The previous figures confirm when the equilibrium has been reached; the rate of change with respect to time was constant and linear. During the time from 0 days to 4 days the line had very steep slopes indicating the initiation steps of the reaction. After four days the plots showed a line with a lower slope indicating that the reaction had reached equilibrium. From these figures it was determined that the time to reach equilibrium was four days. The current density at this time is the corrosion current density i_{corr} . That value will be calculated later in the section 4.6.

4.5 Measurement of the corrosion potential

After the time required to reach equilibrium had been established which is 4 days. The solution, in which the mixture of H_2 and N_2 was bubbled for 5 min, potential of the equilibrium sample was measured using the three electrode apparatus. It is equal to - 0.569 volts. This potential is the corrosion potential E_{corr} .

4.6 Calculated current density(i_d) at the equilibrium time

From the previous calculations the weight of the material converted in the reaction (w) is determined and at the equilibrium time 4 days. Also the current flow (I) can be determined by Faraday's law:

$$W = k \cdot I \cdot t \quad (4.6.1)$$

Also the current density can be calculated at 4 days by the following equation:

$$i_d = I/SA \quad (4.6.2)$$

Where I is the current flow and SA is the surface area. The following table shows the values of current flow and current density at 4 days:

TABLE 4.21 The values of current flow and current density at equilibrium time

Experimental #	I	i_d	$\log i_d$	Initial potential E
1	0.000438	0.000142208	-3.847076606	-0.433
2	0.00044	0.000142857	-3.84509804	0.345
3	0.00039	0.000126623	-3.897486109	-0.5565
4	0.0003652	0.000118571	-3.926019948	-0.565
5	0.0003604	0.000117013	-3.931765934	-0.585
6	0.000277	8.99351E-05	-4.046070947	-0.597
7	0.000204	6.62338E-05	-4.178920549	-0.59
8	0.00034	0.00011039	-3.957071799	-0.557
9	0.00052	0.000168831	-3.772547373	0.412

4.7 The Development of the Evan's Diagram from the Data

The Evan's Diagram for the system is seen below. The Evan's Diagram plots cell potential against the current density as it is shown in the following figure:

FIGURE 4.15 The Evan's Diagram

In the constructed diagram above the Y axis starts at a potential of -0.8 volts and extends to 0.2 volts. This is within the potential range of the hydrogen ion / iron corrosion system as seen in the Pourbaix diagram. In the figure above, the hydrogen potential of the water was adjusted by bubbling a mixture of hydrogen and nitrogen through the water. The initial hydrogen potential was -0.433 volts. A horizontal line is drawn from the Y axis at the value of the hydrogen half potential indicating this upper limit of the corrosion system. An iron coupon was immersed into a bag containing that pretreated water. The iron was corroded because the potential of the half-cell of the hydrogen rich water is more positive than the potential of the iron half cell potential. In this case it is. The iron half-cell potential is taken from the Pourbaix diagram. It has a value of -0.62 v. A horizontal line is drawn at this voltage.

The next value needed for the Evan's diagram construction is the corrosion current. The system was permitted to stand for several two day time periods. Analysis of the data as explained in the previous paragraph showed that after four days the system had reached corrosion equilibrium. From the analysis of the soluble iron in solution the current flow responsible for the reaction was measured. It was shown to be $10^{-4.25}$ amps. When adjusted for surface area the corrosion current density is $10^{-3.89}$ amps. This is the corrosion current density; a vertical line at the corrosion current was drawn from the x axis at this current density on the Evan's diagram.

The potential of that equilibrium solution is the corrosion potential. That potential was measured using the platinum electrodes. That potential is -0.562 volts. A dashed horizontal line is drawn from the Y axis to the corrosion current line on the Evan's diagram. The point of intersection is the equilibrium corrosion condition.

No attempt was made to measure the exchange current or Tafel slope in this research. Difficulties with those measurements in such dilute solutions were discussed in the literature review. The tabular data in Figure 2.20 shows that the Tafel slopes for both the cathodic reaction, the reduction of hydrogen ion to hydrogen gas on an iron surface, and the anodic reaction, the oxidation of iron to ferrous ion on an iron surface, are consistent. Inspection of that table show that the exchange current for the hydrogen gas on an iron surface is also consistent but the exchange current for the oxidation of iron on an iron surface has significant variability. It was decided to use the average Tafel slopes from the Table 2.2 and our data to calculate the exchange currents. Since the Tafel slope represented the rise over run and we have a common point, the corrosion condition; the exchange currents of both reactions can be calculated. These points are designated on the figure above.

The results of this construction show that there is good agreement in the exchange current for the hydrogen reduction on the iron surface, but the exchange current for the oxidation of iron is significantly less than that reported in the table. The corrosion voltage of the iron half-cell potential was validated by back calculation using the soluble iron concentration and the Nernst equation. That value is valid for these dilute solutions.

The Evans' diagram can be used to predict the effect of changing the cell potential on the corrosion rate. Since the exchange currents are fixed values a vertical line can be drawn from the x axis at the exchange current values. By changing the cell potentials horizontal lines can be drawn from y axis at those potentials. At the points where the potential and exchange currents intersect, a new line with the Tafel slope must be drawn. The current value where the anodic line and cathodic line cross is the new corrosion

current density. The value of this current can be used to determine the reaction rate change as a function of change the solution potential. In the experiments done the potential was varied. When the appropriate lines are drawn and the intersection points are defined, the appropriate corrosion currents are determined. The corrosion rates at these potentials agree with those determined by the experimentation.

4.8 Results discussion

There are several individual results that can be ascertained from the data. First by comparing the amount of iron reacted as a result of corrosion it becomes obvious that the presence of hydrogen in the water does reduce the quantity and the rate of production of reacted iron. This can be verified when one compares the histograms for reacted iron of samples with hydrogen gas infused in the water to that sample with nitrogen and carbon dioxide.

Second, it also becomes apparent that the more hydrogen dissolved in the water the less iron reacted. This can be verified when one compares the histogram of the hydrogen infused samples in which the hydrogen was permitted to infuse for a longer time to the histogram of the samples with the lower infusion time. The solution potential decreases as the hydrogen infusion time increases. This would imply that more hydrogen dissolved in the water at longer infusion time. Thus the result would be expected.

Third, when the reaction data is fitted to the linear equations two equations can fit the data. The first line extends from zero days to four days, and the second linear fit extends from four days to sixteen days. The initial line represents the start up of the corrosion system. It would be expected that this line would have the steepest slope of the two lines because the system has not reached the state of “pseudo equilibrium”. It is

interesting to note that the slope for that first line is steepest for the solutions with the highest infusion time of hydrogen.

By using Faraday's law the corrosion currents can be calculated for each of the tested systems. From a measurement of the corrosion potential at the point of equilibrium a Evan's diagram can be prepared. The corrosion current densities for the test can be compared to those expected from the Evan's diagram and these are in good agreement. This established the logarithm of the lowest possible corrosion density as - 5.2. That value is nearly obtained by infusion of hydrogen and hydrogen nitrogen in the water for 20 minutes. In order to further reduce or even eliminate the corrosion of iron pipes hydrogen or hydrogen nitrogen gas would have to be infused in the water at higher pressures. This can be hypothesized because more hydrogen dissolved in water at high pressure. This would be possible since the water is pumped under pressure.

CHAPTER 5

CONCLUSIONS AND RECOMANDATIONS

5.1 Conclusions

- (1) Samples of iron when immersed in water treated with nitrogen and carbon dioxide corroded at rates which would cause significant pollution.
- (2) The infusion of hydrogen in to the water at different times decreased the solution potential and therefore decreased the rate of iron corrosion
- (3) The protection from hydrogen had a longer life than samples infused with a mixture of hydrogen and nitrogen for the same time period.
- (4) A state of pseudo equilibrium for the corrosion of iron in our samples was reached after 4 days.
- (5) The corrosion current density for the test samples and the solution potential can be used to develop an Evan's Diagram. This Evan's Diagram can be used to predict the lower limit of protection of iron by infusion of hydrogen gas. Corrosion current densities calculated for the corrosion data agreed with the Evan's Diagram assessments.
- (6) To eliminate iron corrosion the hydrogen cell potential would have to be made lower than the iron oxidation potential by pressurization of hydrogen to eliminate the reaction and therefore eliminate the iron pollution offensive to the users of the water.
- (7) The hypothesis of this thesis was shown to be correct that hydrogen infusion can reduce the rate of the iron corrosion. But the corrosion of iron can not be eliminated by hydrogen infusion at atmospheric pressure.

5.2 Recommendations

(1) Although the chemistry of the hypothesis for this thesis seems correct and validated by the experiments conducted in this research, a analysis to determine the necessary limits has not be completed. Before the technology can be applied in any form that study needs to be completed.

(2) Hydrogen gas dissolved in water may indeed reduce or prevent but hydrogen also effect steel. It diffuses into steel and caused hydrogen embitterment. This could cause mechanical failures of the pipes. The effect of hydrogen on the properties of the metal need to be evaluated before this technology can be advanced.

(3) The actual material used in the pipe construction needs to be tested. In these experiments the samples were made from plain carbon steel. It is known that the pipes are made from a different alloy. The effects of hydrogen in water on those materials need to be evaluated. Further the effect of hydrogen on already corroded pipes needs to be evaluated.

(4) The electrochemical potential of high pressure systems needs to be made. All tests were run at atmospheric pressure. The results indicate that further inhibition of iron corrosion can only be accommodated at high pressures at which more hydrogen would dissolved in water . The electrochemical potential of hydrogen system at high pressure would have to be measured to determine the exact conditions where the iron corrosion will be controlled.

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