# CHAPTER II

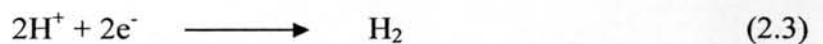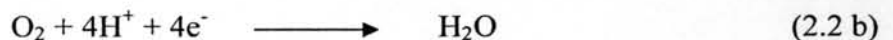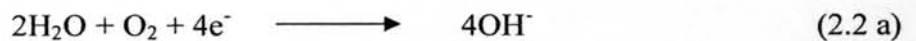## THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 The Basic Theory of Corrosion

Naturally, most metals are found in the forms of oxides, sulphides, carbonates or other complex compounds. To obtain pure metals from their compounds, it is necessary to supply a large amount of energy. The pure metals are usually in high energy states, which are most likely transform to low energy states by recombining with other components in the environment. This phenomenon is known as corrosion, thus a good and clear definition of the corrosion is the deterioration of metal by the reaction with its environment, (National Association of Corrosion Engineer, NACE).

There are 4 essential components present together in the corrosion process. The first one is *anode*, where the oxidation reaction occurs, corrosion takes place and formation of metal ions occurs in reaction (2.1). These ions enter the solution or react with the other chemical species at the interface to form corrosion products.

$$M \longrightarrow M^{n+} + ne^- \qquad (2.1)$$
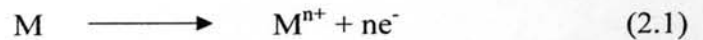
The second component is *cathode* where the reduction reaction takes place by consuming electron released from the anode. Different environment leads to the different types of cathodic reaction. For example, in the presence of oxygen, cathodic reaction is mainly oxygen evolution, reaction (2.2 a) and (2.2 b) in the basic and acid solutions, respectively. In the deaerated-acid solution, the hydrogen evolution is the main cathodic reaction (2.3).

$$2H_2O + O_2 + 4e^- \longrightarrow 4OH^- \qquad (2.2\ a)$$
$$O_2 + 4H^+ + 4e^- \longrightarrow H_2O \qquad (2.2\ b)$$
$$2H^+ + 2e^- \longrightarrow H_2 \qquad (2.3)$$

The reactions at anode and cathode need an electrical connection for currents to flow through, this is called *metallic pathway*. Actually, metallic pathway, anode and cathode are part of the same metal because of the heterogeneity of the metal itself. The last component is *electrolyte*, an electrically conducting solution.

2.2 Corrosion in Oil and Gas Production

Koch *et al.* (2002) estimated the total annual cost of corrosion in the oil and gas production industry in the united state of 1.372 billion dollars, which could be broken down into 589 million dollars in surface pipeline and facility costs, 463 million dollars annually for down hole tubing expenses, and 320 million dollars for capital expenses related to corrosion.

Approximately 35% of failures in the oil and gas production come from corrosion which not only decreases the production rate, but also increases repair cost and the security and environmental problems. The corrosion takes place if the 3 parameters are present together, i.e. liquid water, corrosive agent (i.e. CO_2, H_2S, O_2, Cl_2 and organic acid) and heterogeneities (in the electrolyte, metal matrix and on the metal surface). The corrosion can be accelerated by these parameters: temperature, salts, flow effects, sand, and human impact (bacteria or bad design and construction). In order to prevent the corrosion, 7-10% of capital expense is spent to build the facilities such as dehydration unit and 5-15% of operation expense is charged for corrosion inhibition, Gunaltun (2006).

2.2.1 Corrosion in Oil and Gas Equipment

The main corrosion areas are artificial lift wells, casing and tubing, surface equipment, and enhanced oil recovery operations.

2.2.1.1 Artificial Lift Wells

The most common form of artificial lift well is a sucker rod pumping system (the other forms are electric submersible pumps and gas lift systems). The major components of sucker rod pumping systems include the pump,

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the tubing and the sucker rod itself. Corrosion occurs in this equipment results in the plugging of marginal wells.

2.2.1.2 Casing and tubing

For external casing, corrosion occurs because it exposes to the water. Cementing the casing can prevent some of the corrosion. Inside the casing, corrosion in the annulus between the casing and the tubing depends on the type of fluid. Packer fluids, usually composed of drilling mud, brine and produced oil or gas, can be designed to meet the corrosion mitigation requirements of a particular well. Without packer fluids, the annulus space is filled with wet gas. That can cause the corrosion if acid gasses are present in the production well.
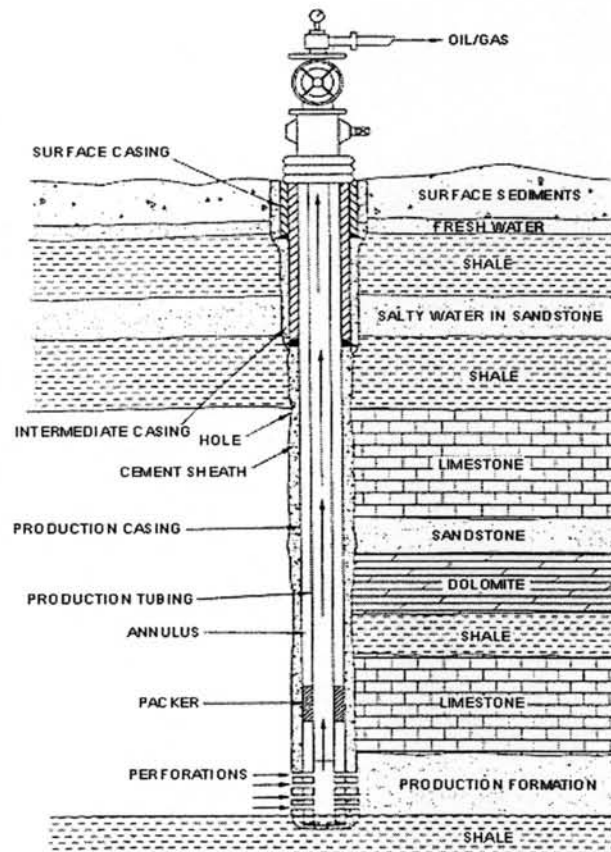

Figure 2.1 Typical production tubing and casing (Manocha *et al*, 1999).

2.2.1.3 Surface Equipments

Corrosion can take place in three parts of surface equipments, i.e. storage tanks, wellheads and flow lines.

Storage tanks can be damaged by both internal and external corrosion. Internal corrosion often occurs at the inside top of the tank, causing from oxygen or hydrogen sulfide gas, and at the bottom of the tank, resulting from salt water or solids settling. For external corrosion, it is usually found at the bottom of the tank, or the parts of the tank contacting with water or wet soil. Methods for controlling external corrosion on storage tanks include cathodic protection, coatings and foundations.

Wellheads and christmas tree equipments are encountered to corrosion especially in high pressure and high velocity gas wells.

Flow lines can be corroded due to the presence of water. Half bottom side is corroded as it is in contacting with the water (settling due to the gravity). The top surface is not corroded as it is in contacting with oil. The layout and sizes of the flow lines can be designed to minimize corrosion. In addition, inhibitors or coatings are also used for mitigating corrosion in these lines. For lines buried under the surface, differential aeration is also a source of corrosion. Differential aeration is one section of the metal exposed to oxygen while the left is not. The section with no aeration becomes anodic, and is subject to preferential corrosion.

Enhance oil recovery operation is an important process to recover oil production rate due to the decrease in the reservoir pressure along the production period. Treated sea water or produced water is injected into the reservoir. Sometimes, CO_2 is also found to be injected into the reservoir as the same reason. One more complex approach is a water-alternating-gas (WAG) injection, in which water and gas are alternately injected into the well. This type of process requires that the equipment is able to handle corrosion from both water and gas.

2.2.2 Carbon Dioxide Corrosion

The corrosion in oil and gas production can be classified into 2 different types, external and internal corrosion. The external corrosion is caused by

external environment such as sea/ground water, soil and atmospheric. The internal corrosion is caused by produced effluents, i.e. CO_2, H_2S, organic acid and solid particles etc. and injected effluents, i.e. produced water etc. The internal corrosion is considered to be more dangerous because of the difficulty in protection and inspection methods. Most of the time, internal corrosion takes place inside the production tubing, which is caused by the various chemicals from the reservoir. Since inside the reservoir is absence of oxygen, the main corrosive gases are carbon dioxide and hydrogen sulphide.

2.2.2.1 Source and mechanism of carbon dioxide corrosion

Normally, CO_2 presents in flowing wells, gas condensate wells, areas where water condenses, tanks filled with CO_2, saturated produced water and flow lines. CO_2 can corrode by itself or in a form of carbonic acid by reacting with water. The most common forms of CO_2 corrosion are uniform corrosion and pitting corrosion. CO_2 corrosion products include iron carbonate (siderite, $FeCO_3$), iron oxide, and magnetite. Corrosion product colors may be green, tan, or brown to black. There are uses of caustic soda to control pH in drilling process or corrosion inhibitors in producing wells and flow lines to reduce or prevent corrosion in CO_2 environment.

The behavior and mechanism of carbon dioxide corrosion are as followings. Firstly, gaseous carbon dioxide reacts with the liquid water to form weak carbonic acid.

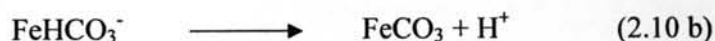$$CO_2 + H_2O \longrightarrow H_2CO_3 \qquad (2.4)$$

The subsequent corrosion process is controlled by three cathodic reactions and one anodic reaction. The cathodic reactions show in reactions (2.5) – (2.7). At the beginning, carbonic acid is reduced to bicarbonate ions and carbonate ions, respectively. Protons from reactions (2.5) and (2.6) are consumed in the hydrogen reduction. Besides, an anodic reaction is the oxidation of metal providing metal ions as shown in reaction (2.8).

$$H_2CO_3 + 2e^- \longrightarrow H^+ + HCO_3^- \qquad (2.5)$$

$$HCO_3^- + 2e^- \longrightarrow H^+ + CO_3^{2-} \qquad (2.6)$$

$$2H^+ + 2e^- \longrightarrow H_2 \qquad (2.7)$$

Heuer *et al* (1999) suggested that the CO_2 corrosion occurs in anaerobic condition, so there is only the oxidation of iron to ferrous ion (Fe^{2+}) and iron carbonate has high probability to be produced as a corrosion product.

$$Fe \longrightarrow Fe^{2+} + 2e^- \qquad (2.8)$$
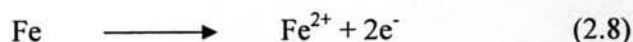
Ferrous ions can be directly reacted with carbonate ions, as given in reaction (2.9) or reacted with bicarbonate ions to form complex, $FeHCO_3^-$, (2.10a) which the complex dissociate further to give the final product, iron carbonate as given in reaction (2.10 b).

$$Fe^{2+} + CO_3^{2-} \longrightarrow FeCO_3 \qquad (2.9)$$

$$Fe^{2+} + HCO_3^- \longrightarrow FeHCO_3^- \qquad (2.10\ a)$$

$$FeHCO_3^- \longrightarrow FeCO_3 + H^+ \qquad (2.10\ b)$$

The properties of iron scale layer and its influence on the corrosion rate are important for studying the corrosion behavior. The protectiveness of the surface scale depends on the nature of base alloy (composition and microstructure) and the properties of the environment. The protective corrosion scale can behave like a barrier to protect the metal under the scale. Brondel *et al* (1994) suggested that iron carbonate or siderite itself can be soluble but it can be protective under some conditions, i.e. elevated temperature, higher pH and lack of turbulence.

2.2.2.2 *Factors affecting the corrosion behavior*

The corrosiveness of the environment is a function of numerous parameters such as water chemistry, gas/fluid velocity, CO_2 content, and temperature (Lopez *et al*, 2003).

Temperature

In most of the reactions, higher temperature leads to higher reaction rate kinetically, however it still depends on many other parameters. Gas solubility shows significant effect on corrosion rate as described in reaction (2.4). It is decreased when temperature is increased. The formation of carbonic acid is strongly depending on the solubility of carbon dioxide in liquid water.

Cui *et al.* (2006) studied the influence of temperature of pipeline steel type N80, J55 and P110 in simulated produced water saturated with super-critical carbon dioxide and found that corrosion scale forming on the surface was compact and has an important role on the corrosion behavior when temperature was increased as shown in Figure 2.2. Lopez *et al* (2003*)* suggested that the corrosion proportionally increased with temperature below 60°C until reaching the maximum corrosion. Temperature at this point is known as scaling temperature. Further increase in the temperature above the scaling temperature, the corrosion rate was decreased. In contrast, this temperature depends on the flow rate, CO_2 partial pressure and among other factors.
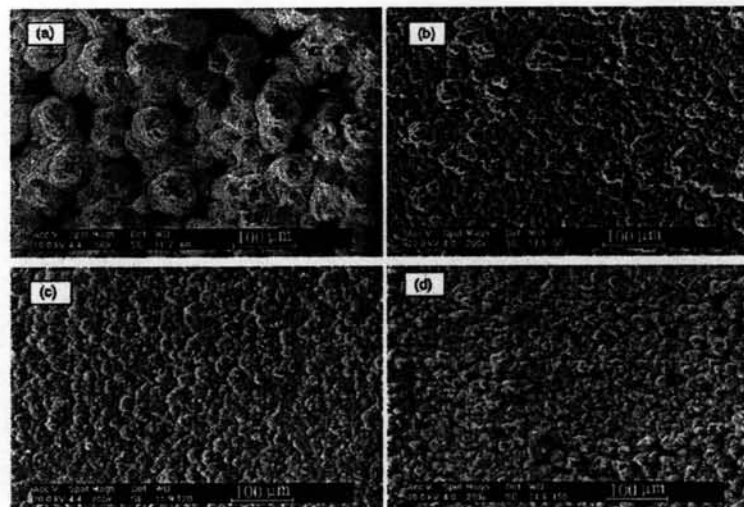

Figure 2.2   SEM images of corroded surface of J55 samples immersed in static simulated produced water saturated with supercritical-CO_2 for 96 h at a) 60°C, b) 90°C, c) 120°C, and d) 150°C, (Cui *et al*, 2006).

Chloride

Chloride ions, basic anions present in produced water (defined as water that presents in the reservoir in a liquid form comprising of various chemicals), has a significant effect on corrosion. At low concentration (0-3% NaCl), the corrosion rate increases with increase amount of NaCl due to enhancement of the conductivity of solution. However, further increase the concentration of NaCl (above 3%NaCl), the corrosion rate gradually decrease because the solubility of oxygen is decrease.

Vourlias *et al* (2004) studied the corrosion mechanism under accelerated atmospheric condition in a salt spray chamber with 5%wt NaCl solution as a corrosive medium. The specimens, aluminum, copper, carbon-steel St-37, stainless steel 304 and galvanized steel were examined after 4 and 12 days by SEM and XRD technique. In the case of aluminum, Al_2O_3 was formed in very short period to protect the substrate from further corrosion. However, chloride ions could penetrate and destabilize the oxide film and lead to pitting corrosion. Copper seemed to be corroded uniformly and corrosion products of Cu(I) such as Cu_2O (Cuprite) and Cu(II) chlorides were found at the initial stage. After that, the new corrosion products such as Cu(OH)Cl or other Cu^{2+} compounds were formed. Chloride ions also penetrate into protective layer of copper to cause a pitting corrosion as in aluminum. In the case of stainless steel, it seems that a barrier mainly consists of iron-chromium oxides. Chloride ions still penetrated through the protective film but as not deep as aluminum and copper. For galvanized steel whereas ferrous substrate is protected by zinc coating, the chloride ions penetration is very intense.

Hardness of solution

Calcium and magnesium cations are also found in the sea water. They are less corrosive because a protective calcium and/or magnesium carbonate film are formed on the metal surface via carbon dioxide dissolution.

$$Ca^{2+} + 2HCO_3^- \longrightarrow Ca(HCO_3)_2 \longrightarrow CaCO_3 + CO_2 + H_2O \qquad (2.11)$$

Jiang *et al* (2006) studied the effect of $CaCl_2$ in simulated seawater to understand the carbon steel corrosion in the stagnant and flowing condition of 4-6% NaCl solution saturated with CO_2 at 57°C. The corrosion rate increased with the increase of Cl⁻ but the corrosion rate decreased when Ca^{2+} was added due to the formation of thick protective film of $CaCO_3$. However, the accumulation of this film results in a decrease in diameter of pipeline.

2.2.3 Corrosion by Hydrogen Sulfide

The major problem in the presence of H_2S is metal embrittlement caused by penetration of H_2 in the lattice metal. Hydrogen sulfide is a weak acid when dissolved in water. It generates H^0 which can penetrate or absorb in steel surface, promoting sulfide stress cracking (SSC) in high strength steels and fractures in the equipment.

The most common corrosion types are uniform corrosion, pitting corrosion, corrosion fatigue, sulfide stress cracking, and hydrogen blistering and hydrogen embrittlement. Corrosion products include black or blue-black iron sulfides, pyrite, greigite, mackinwaite, kansite, iron oxide (Fe_3O_4), magnetite, sulfur (S), and sulfur dioxide (SO_2). In order to reduce or prevent corrosion from H_2S, high pH is required in the drilling process or using corrosion inhibitors in producing wells and flow lines.

Ma *et al* (1999) suggested that hydrogen sulfide (H_2S) can either accelerate or inhibit corrosion of iron under different experimental conditions. In most cases, H_2S accelerate the corrosion on the anodic iron dissolution and the cathodic hydrogen evolution causing the iron to be corroded in acidic medium. However in the case of low concentration of H_2S ($\leq$ 0.04 mmol dm^{-3}), pH value of electrolyte solution of 3-5 and the immersion time over 2 hours, H_2S can strongly inhibit the corrosion by forming the protective film, ferrous sulfide (FeS) on the electrode surface. The structure of ferrous sulfide film is converted into troilite and pyrite with the greater stability and the more protective property.

2.2.4 Oxygen Corrosion

Even the oxygen is not present in the reservoir, it can contaminate at the top of tubing, i.e. through leakage of pump seals, casing etc. When oxygen removal processes such as gas stripping and chemical scavenging are failed, oxygen contamination gets in waterflood systems. Oxygen dissolved in water is one of the primary causes of corrosion in the oil field. Oxygen is a strong oxidant which reacts quickly with metal creates the most common types of corrosion include pitting corrosion and uniform corrosion.

In the presence of oxygen (greater than 40 ppb), an unstable corrosion product, $FeCO_3$, is oxidized to ferric (Fe^{3+}) and the rate of cathodic reaction (2.12) increase as increase concentration of oxygen.

$$2H_2O + O_2 + 4e^- \longrightarrow 4OH^- \qquad (2.12)$$

The oxidation can be avoided by keeping oxygen concentration to below 40 ppb. Oxygen removal may be done by mechanical and chemical means. Mechanical means including gas stripping and vacuum deaeration while chemical means include sodium sulfite, ammonium bisulfite and sulfur dioxide.

2.2.5 Mercury Corrosion

Mercury is another interesting component. Less attention has been paid on its influence on the corrosion in the natural gas production. Mercury exists in the reservoir in many forms; e.g organic mercury, inorganic mercury, etc. Generally, its concentration in the Gulf of Thailand is between 3-6 ppm.

The implication of the effects of mercury in natural gas was not reported until 1973, when a catastrophic failure of aluminum heat exchangers occurred at the Skikda liquefied natural gas plant in Algeria and in the gas gathering system of Groninger field in Holland (Spiric, 2001).

The mechanism of all corrosion caused by the presence of metallic mercury takes place in the following sequences (Leeper, 1969).

- Elemental mercury amalgamates with the surface layer of the metal being corroded.
- The minute amount of the base metal alloyed with the elemental mercury is exposed intimately in an un-passivated state to the action of the corroding medium or, to state it alternatively, a short-circuited corrosion cell is formed between the mercury and the base metal with liquid water as an electrolyte.
- If only pure water is present with inert gases, the base metal in the amalgam is corroded gradually by reaction with water (reaction (2.13)).

$$3\ Fe + 4H_2O \longrightarrow Fe_3O_4 + 4H_2 \qquad (2.13)$$

If an acid anhydride, such as CO_2 or H_2S is present, the corrosion product is the metal carbonate or sulfide.

Although the concentration of mercury in the natural is considered to be very low, Audeh *et al* (1996) observes that its effect is cumulative as it gradually amalgamates with the surface layer of the metal it contacts.

In addition, not only the elemental mercury is corrosive, but other species is also harmful. For example, with the higher in electrode potential (Table 2.1), mercury(II) is considered as a powerful oxidizing agent. When it receives electrons from the base metal, the elemental mercury is formed. Consequently, the corrosion as contended by Leeper is taken place.

Table 2.1 The standard electrode potential of hydrogen ions and mercury ions

Half-reaction	Electrode potential (V)
$2H^+ + 2e^- \rightarrow H_2$	0
$Hg^{2+} + 2e^- \rightarrow Hg$	+0.788

2.2.6 Materials in Oil and Gas Industry

Steels are mostly used as structural materials in oil and gas industry. Mild steel or low carbon steel is the most versatile due to its mechanical strength, easy manufacture, formability, weldability and low cost. However, in an aggressive environment, carbon steel can not be sufficient and then stainless steels are found to be more suitable. There are various types of steels depending on its composition, manufacture methods, finishing methods, microstructure etc.

2.2.6.1 Carbon Steel

Carbon steel is a metal alloy composed of two elements, iron and carbon, where other elements are present in trace amount to improve some properties. The only other alloying elements allowed in plain-carbon steel are: manganese (1.65% max), silicon (0.60% max), and copper (0.60% max). Steel with low carbon content has the same properties as iron, soft but easily formed. As carbon content increases, the metal becomes harder and stronger but less ductile and more difficult to weld.

Carbon steel is the most widely used material. It accounts for approximately 85% of the annual steel production worldwide. Despite its relatively limited corrosion resistance, carbon steel is used in large tonnages in marine applications, nuclear power and fossil fuel power plants, transportation, chemical processing, petroleum production and refining, pipelines, mining, construction and metal-processing equipment. Usually, carbon steel can be classified according to the variations of carbon content which have strong effect on the properties of carbon steel. The properties of carbon steels are depended on the percent of carbon content. The increasing in carbon content leading to increased hardness and strength.

2.2.6.2 Stainless steel

Stainless steels are iron-based alloys containing at least 12% chromium. Stainless steels are commonly divided into six groups, martensitic stainless steels, martensitic-austenetic stainless steels, ferritic stainless steels, austenitic stainless steels, duplex (ferritic-austenitic) stainless steels, and

precipitation-hardening stainless steels as summarized in Table 2.2. The corrosion is decreased as percent of chromium is increased (Figure 2.3). As chromium is added to the steel, a rapid reduction in corrosion rate is observed to around 10%Cr because of the passive layer. In order to obtain a compact and continuous passive film, chromium content of at least 12% is required.

Table 2.2 Composition ranges for different stainless steel categories (Leffler, 2001)

| Steel category	Composition (wt%)					Hardenable	Ferro-magnetism
	C	Cr	Ni	Mo	Others		
Martensitic	>0.10	11-14	0-1	-	V	Hardenable	Magnetic
Martensitic-	<0.1	12-18	4-6	1-2		Hardenable	Magnetic
Precipitation-		15-17	7-8	0-2	Al	Hardenable	Magnetic
Ferritic	<0.08	12-19	0-5	<5	Ti	Not	Magnetic
Ferritic-austenitic	<0.05	18-27	4-7	1-4	N, W	Not	Magnetic
Austenitic	<0.08	16-30	8-35	0-7	N, Cu, Ti,	Not	Non-
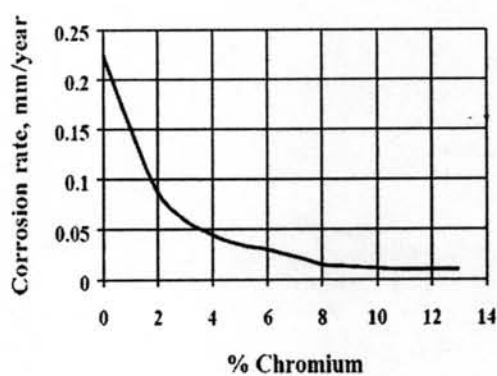
Figure 2.3 The effect of Chromium content on corrosion rate of material (Leffler, 2001).

Reactions (2.14) and (2.15) can be expressed for the mechanism of chromium oxide formation in the presence of oxygen and water (Nivitchanyong).

$$Cr \longrightarrow Cr^{3+} + 3e^{-} \qquad (2.14$$

$$aCr^{3+} + bH_2O + cO_2 \longrightarrow Cr_xO_y(OH)_z \qquad (2.15$$
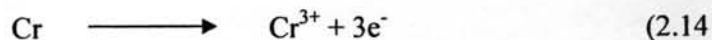
The arrangement of chromium oxy hydroxide is alike a network covering the surface as demonstrated in Figure 2.4 leading to the formation of protective thin film with a thickness of 10 nm. Therefore, the uniform corrosion is prevented or slowed down due to the presence of such film. However, in some condition, the presence of chloride ions can cause the breakage of the film by attacking at particular area, which can be further developed to the pitting corrosion or crevice corrosion.
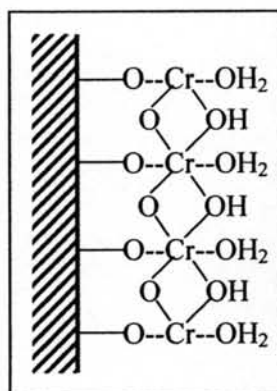
Figure 2.4 Arrangement of chromium oxide film on stainless steel surface (Nivitchanyong)

The applications and selection of stainless steels are usually based on corrosion resistance, fabrication characteristics, availability, mechanical properties in specific temperature ranges and product cost. However, corrosion resistance and mechanical properties are usually the most important factors in selecting a grade for a given application. Mechanical properties such as strength,

high-temperature strength, ductility and toughness, are thus also important. Carbon is determined as a strong austenite former by promoting austenite structure which increases the mechanical properties of steels. Figure 2.5 shows relationship between stress and strain of some stainless steels. For example, martensitic grade stainless steel having the highest stress contains carbon content at least 1% which is the highest among other steels.

Other elements are also added to improve stainless steel characteristics including nickel, molybdenum, copper, titanium, aluminum, silicon, niobium, nitrogen, sulfur, and selenium.
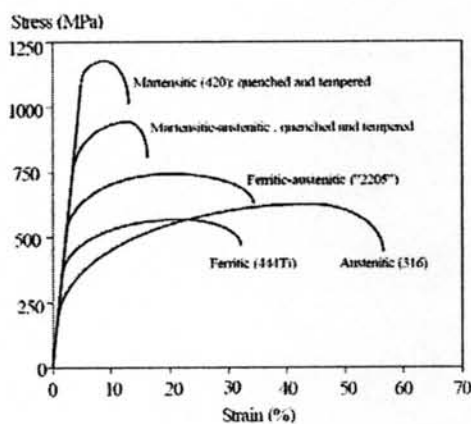
Figure 2.5 Stress-Strain curve for some stainless steels (Leffler, 2001).

Zhang *et al* (2005) revealed that 13Cr martensitic stainless steel is widely used in oil and gas field containing CO_2 due to good corrosion resistance in CO_2 environments and lower cost compared with other stainless steel such as duplex stainless steel. Fontana (1986) suggested that martensitic grade stainless steels are usually used in applications requiring moderate corrosion resistance plus high strength or hardness.

2.3 Application of Thermodynamic to Corrosion

Most of metals used in everyday life are extracted from ores, e.g. metal oxides, metal sulfides and/or metal carbonates etc. The extract process is the addition of energy, usually heating, to break initial chemical bonds and form metal-metal bonds. Thus, pure metals are usually in a high energy state compared to those ores. Hence, there is high tendency for converting pure metal to low energy state by combining with chemicals present in the environment. Thermodynamics give an understanding in the energy change of the corrosion process and possibly show conditions to prevent the corrosion. However, the rate of corrosion governed kinetic laws can not be predicted by thermodynamics.

2.3.1 Nernst Equation

An equation correlating chemical energy and the electric potential of a galvanic cell or battery is Nernst equation. An example of Nernst equation of Fe and Cu is demonstrated by the iron plate being immersed in a solution containing copper (II). After about 10 minutes, the iron becomes coated with copper and concentration of iron (II) in the solution is increased. The effect is so called replating.

Half-reactions which show how electrons are produced and consumed can be expressed as shown in reactions (2.16) and (2.17) for iron and copper, respectively.
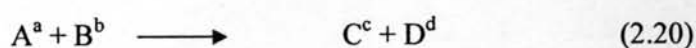
$$Fe \longrightarrow Fe^{2+} + 2e^- \qquad (2.16)$$

$$Cu^{2+} + 2e^- \longrightarrow Cu \qquad (2.17)$$
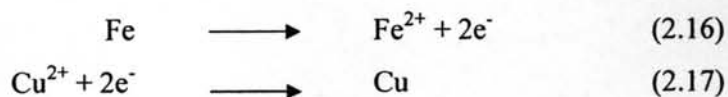
The complete effect is represented by combining of two reactions as shown in reaction (2.18).

$$Fe + Cu^{2+} \longrightarrow Fe^{2+} + Cu \qquad 2.18)$$
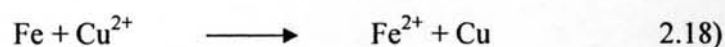
To calculate the value of free energy change of the reaction, ΔG, the following thermodynamic equation is used.

$$\Delta G = \Delta G^o + RT \ln J \qquad (2.19)$$

Where, for a reaction

$$A^a + B^b \longrightarrow C^c + D^d \qquad (2.20)$$

J is defined as

$$J = \frac{[C]^c [D]^d}{[A]^a [B]^b} \qquad (2.21)$$

Thus, free energy change of the case of copper/iron becomes

$$\Delta G = \Delta G^o + RT \ln \frac{[Fe^{2+}][Cu]}{[Cu^{2+}][Fe]} \qquad (2.22)$$

However, this value can be related to the electrical potential and flow of currents by using equation (2.23), which is known as Faraday's Law.

$$\Delta G = (-zF)\Delta E \qquad (2.23)$$

Where F is Faraday's constant, 96,494 coulombs per mole, which represents the charge transported by 1 mole of electrons. E, potential, is measured in volts and z is the number of electrons transferred. In this case, z is equal 2 for iron and copper.

Therefore, ΔG and ΔG^o in equation (2.22) are substituted by $(-zF)E$ and $(-zF)E^o$,

$$\Delta E = \Delta E^{o} - \frac{RT}{zF} \ln \frac{[Fe^{2+}]}{[Cu^{2+}]} \qquad (2.24)$$

It is noted that the concentration of solid substances, Fe and Cu, is usually taken as unity. Consequently, the numerical values of constants ($R = 8.3143$ J mol^{-1} K^{-1}, T = 298 K and F = 96,494 coulombs per mole) are introduced into the equation (2.24) together with conversion to the based 10-logarithmic.

$$\Delta E = \Delta E^{o} - \frac{0.059}{z} \log \frac{[products]}{[reactants]} \qquad (2.25)$$

Equation (2.25) is known as the **Nernst Equation** which is usually used in the form of equation (2.26)

$$\Delta E = \Delta E^{o} + \frac{0.059}{z} \log \frac{[Oxidized]}{[Reduced]} \qquad (2.26)$$

It is obviously seen that the potential of any electrodes is depended on the concentration of ions containing in such the solution. For the reaction of iron (reaction 2.16), equation (2.26) is reduced to equation (2.27). Since the standard electrode potential, E^0 is -0.44 V at 25°C, the anodic reaction can becomes more active only when Fe^{2+} is very low. On the contrary, if concentration of Fe^{2+} near the surface is greater than the bulk concentration, the potential of electrode becomes higher and the electrode becomes noble.

$$E = E^{o} + \frac{0.059}{2} \log[Fe^{2+}] \qquad (2.27)$$

2.3.2 Pourbaix Diagram or Electrode potential-pH Diagram

The Pourbaix diagram is a graphical representation derived from Nernst's equation showing regions of thermodynamic stability of species in metal-

water electrolyte systems. It may be thought as a map showing conditions of solution oxidizing power (potential) and acidity or alkalinity (pH) for the various possible phases that are stable in an aqueous electrochemical system.

Normally, Pourbaix diagrams of metal are divided in to 3 regions, immune, passive and corrosion region as shown in Figure 2.6. The corrosion is possible only in the corrosion region where the stable forms are soluble ions, e.g. Fe^{2+}, Fe^{3+} or $HFeO_2^-$ etc. The immune region is the region where the stable form is the reduced to metal itself, i.e. Fe, the metal is said thermodynamically immune to corrosion as shown the bottom region of Figure 2.3. Passive region is a preferable form of metal oxide film. The passivity is the characteristic corrosion resistance due to the presence of passive oxide film that can protect the metal from the surrounding solution.
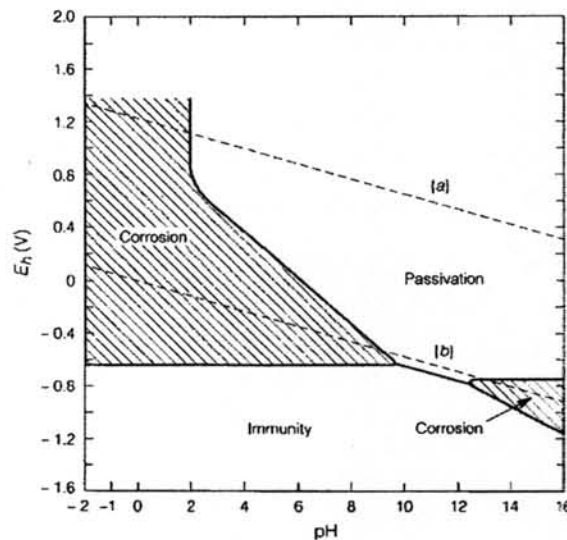

Figure 2.6 The schematic of Pourbaix diagram for metal (Tretheway *et al*, 1988).

The main uses of the diagrams are to predict the spontaneous direction of reaction, composition of corrosion products and environmental changes that will prevent or reduce the corrosiveness of solution.

The Pourbaix of iron-water is shown in Figure 2.7. In the diagram, the

horizontal lines, (1) and (2), represent the pure electron transfer reaction, described in reactions (2.28) and (2.29), which are solely dependent on potential but independent of pH.

$$Fe \longrightarrow Fe^{2+} + 2e^- \tag{2.28}$$

$$Fe^{2+} \longrightarrow Fe^{3+} + e^- \tag{2.29}$$
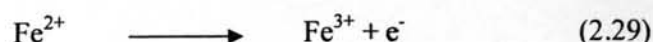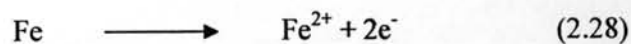
These lines spread across the diagram horizontally until the pH is high enough to facilitate the formation of hydroxides, represented by vertical lines which are corresponded to reactions (2.30) and (2.31).
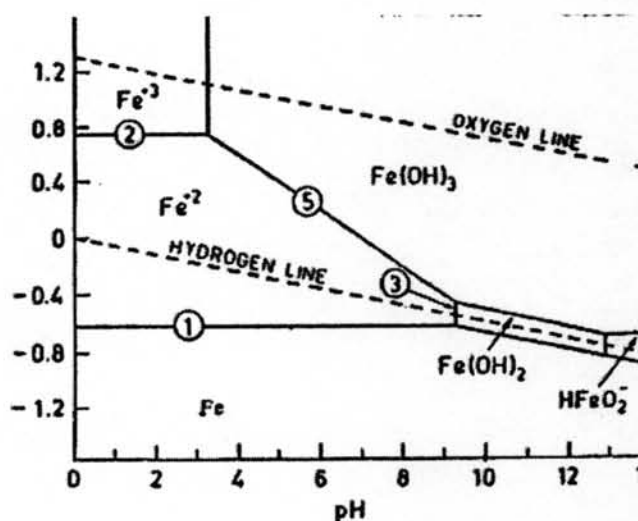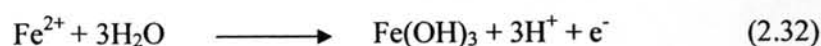

Figure 2.7 Pourbaix diagram for iron-water system (Chatterjee *et al*,2001).

The equilibrium reaction involving both electron transfer and pH are represented by the sloping lines, reactions (2.32) and (2.33). In Figure 2.4, both effective corrosion prevention methods can be thermodynamically achieved. First, the *cathodic protection*, the concept of this technique is to make the iron to be stable in the immune region by lowering the electrode potential to be lower than -0.44 V. Second, *the anodic protection* is achieved by increasing the pH of the solution to reach the passive region. This later technique does not stop the corrosion of iron

because the iron is already corroded and then forms the protective corrosion product, i.e. $Fe(OH)_2$, to delay further corrosion.

$$Fe^{2+} + 2H_2O \longrightarrow Fe(OH)_2 + 2H^+ \qquad (2.30)$$

$$Fe^{3+} + 3H_2O \longrightarrow Fe(OH)_3 + 3H^+ \qquad (2.31)$$

$$Fe^{2+} + 3H_2O \longrightarrow Fe(OH)_3 + 3H^+ + e^- \qquad (2.32)$$

$$Fe + 2H_2O \longrightarrow HFeO_2^- + 3H^+ + 2e^- \qquad (2.33)$$

There are a number of limitations the Pourbaix diagrams. First, they cannot be used for predicting the rate of reaction and the formation of corrosion product, which lead to the passivity. Second, it may not always be true because the oxide may not precipitate on the metal surface. Finally, the pH at the metal surface may vary drastically due to the side reactions, thus prediction of corrosion based on the bulk pH may be misleading.

2.4 Electrochemical Kinetics of Corrosion

Thermodynamically, corrosion is possible in many conditions, but it does not provide the information how fast the corrosion is. Since corrosion occurred in an aqueous solution is governed primarily by an electrochemical reaction, understanding the basic of electrochemical kinetics of corrosion is essential to determine the corrosion process and estimate the corrosion rate.

When the different materials connect together and immersed in a solution, at equilibrium, the potential between these two materials is called open-circuit potential (OCP). Potential drives the electrons to flow from anode to cathode. When the external potential is applied, the flow rate of electrons is changed and the potential of the electrodes is no longer be at the equilibrium. The deviation from the equilibrium potential or OCP is called *polarization*. Electrochemical polarization is divided into two main types, activation and concentration polarization.

The activation polarization refers to electrochemical reactions that are

controlled by a slow step in the reaction sequence, e.g. electron transfer step and/or hydrogen formation step as presented in Figure 2.8 a).

The concentration polarization refers to the reactions that are controlled by the diffusivity of hydrogen ions or other component to be reacted at the surface of material. Figure 2.8 b) illustrates the concentration gradient of hydrogen ion during the hydrogen evolution. At low reduction rate of hydrogen evolution or high diffusion rate of hydrogen ion (as shown in the left hand side), the concentration of hydrogen at the surface is considered to be constant. In the opposite way, when the rate of reduction is greater than the diffusion, the surface becomes lack of hydrogen ions and finally the hydrogen evolution is decreased.

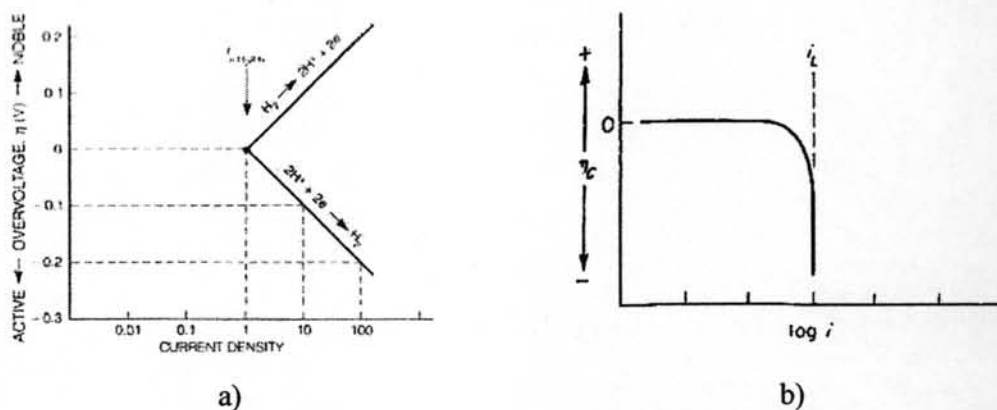a)   b)

Figure 2.8 a) Activation polarization curve of hydrogen electrode and
b) concentration polarization curve (reduction process) (Fontana, 1986).

Usually, activation and concentration polarizations occur together at the electrode depending on the limiting step. The total polarization of the electrode is the summation of activation and concentration polarizations as shown in Figure 2.9. The straight line is known as tafel slope which is useful for corrosion rate calculation.
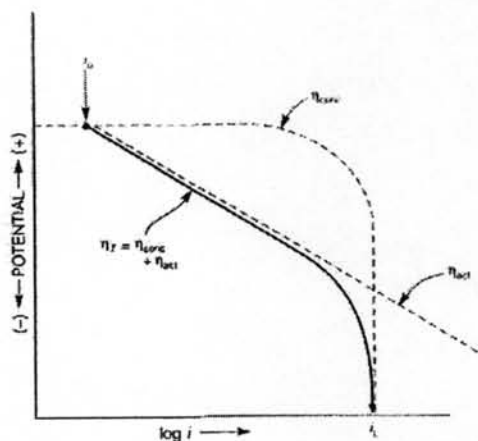
Figure 2.9 Combined polarization: sum of activation (η_{act}) and concentration (η_{conc}) polarizations (Uhlig *et al*, 1991).

The examples of polarization curves are presented in Figure 2.6 where the top curves with the downward slope indicate cathodic reactions. In Figure 2.10 a) shows anodic and cathodic reactions controlled by activation polarization only. A typical example is a well-stirred acid solution. The lower line refers to the hydrogen evolution while the higher one shows oxygen evolution. Obviously, the corrosion rate in the presence of oxygen is higher than that in the hydrogen only. In Figures 2.10 b) and c), the effects of polarization are due to the diffusion controlling on cathodic and anodic, respectively. The limitation in diffusion on cathodic side may be caused by a low concentration of oxygen from the bulk solution. In case of c), anodic limitation may be resulting from slow diffusion of ferrous ions away from the anode. To paraphrase, corrosion rate can be enhanced by stirring the solution in the case of diffusion control limitation. Typically, anode and cathode sites of polarization curve shown in Figure 2.10 d) are separated by the presence of corrosion product and/or solution with some resistance.
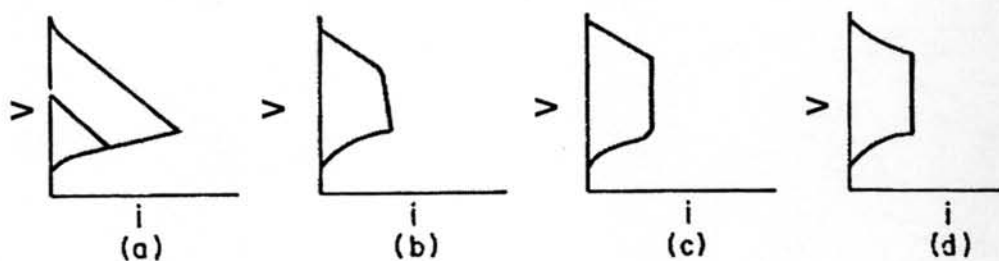
Figure 2.10 Evans-type polarization curves under: a) activation control, b) diffusion control of cathodic reaction, c) diffusion control of anodic reaction, and d) resistance polarization (Tretheway et al, 1988).

2.4.1 Potentiodynamic Polarization Technique

Polarization methods such as potentiostaircase, cyclic voltammetry and potentiodynamic polarization are often used for laboratory corrosion testing. These techniques can provide significant useful information of corrosion mechanisms, corrosion rate and susceptibility of specific materials to corrosion in the designated environments. Polarization methods involve changing the potential of the working electrode and monitoring the current, which is produced as a function of time or potential.

Potentiodynamic polarization is a technique where the potential of the electrode is varied at a selected rate by application of a current through the electrolyte solution. It is probably the most commonly used polarization testing method for measuring corrosion resistance. Figure 2.11 shows the hypothetical polarization curve of stainless steel, combination of two regions, cathodic and anodic regions.

Cathodic polarization is firstly conducted by increasing the potential of electrode from cathodic region to open-circuit potential. Electrons are supplied to the material surface and consumed in the cathodic reaction, e.g. hydrogen evolution or electrodeposition. Further increase potential leads to the decreasing in absolute value of current density. Once the potential reaches the *corrosion potential*, the current density is then increased and anodic region is begun. The intersection between these two regions is obtained at potential and current density known as

corrosion potential (open-circuit potential, E_{corr}) and corrosion current density (i$_{corr}$). In anodic region, where the potential is changed toward positive direction, the electrons are withdrawn from the electrode.

Normally, the higher the potential is applied, the higher the current is obtained. However, for materials present the passive layer, i.e. stainless steel, current density is dropped again at *passivation potential (E_{pp})* and *critical current density(i$_{cc}$).* As the passive film is totally formed on the surface, the current density is constantly equal to *passive current density (i$_p$)* at any potential in the passive region. Further increase the potential to the *pitting potential (E_{pit}),* the passive film is suddenly broken and current density is sharply increased. For materials without passive film formation, the current density continuously increases with potential where the passive region does not present in the polarization curve.
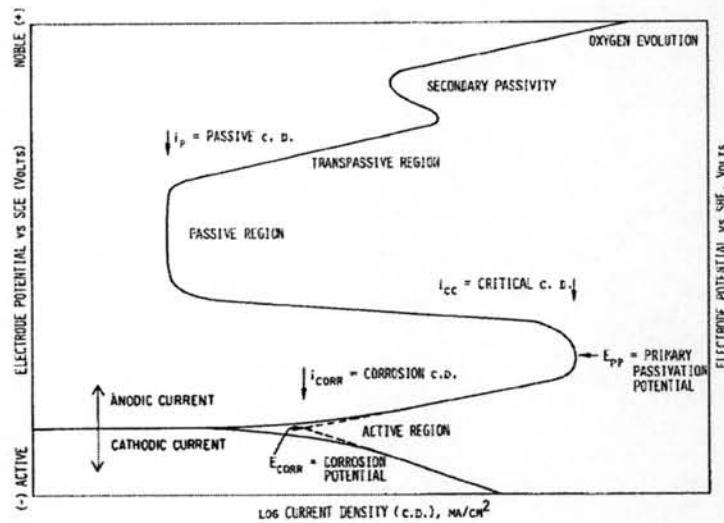

Figure 2.11 The hypothetical diagram of polarization curve of stainless steel (Fontana, 1986).

2.4.2 Three-Electrode Cells and E/log i Plot

A standard laboratory apparatus for measurements consists of three electrodes, working, counter (auxiliary) and reference electrode. The schematic of instrument set up is shown in Figure 2.12.

The working electrode is the electrode being investigated or sample specimen. Figure 2.13 shows the conventional designs of testing equipment where the constant surface area of the specimen is exposed to the solution.

The counter (auxiliary) electrode is used only to make a connection to the electrolyte so that a current can be applied to the working electrode. The counter electrode is usually made of an inert material, such as a noble metal or graphite, to keep it from dissolving. Usually a carbon rod is used, but it can be any material that will not contaminate the solution. Platinum and gold can also be used.

The reference electrode is used to provide a stable datum which the potential of the working electrode can be measured. The most convenient reference electrode to use in an experiment is a saturated calomel electrode (SCE). This electrode is normally linked to the solution via a salt bridge, Luggin capillary, which is saturated KCl solution.

The last component, source of potential change, is potentiostat which applies the potential to the working electrodes so that the current can be measured.
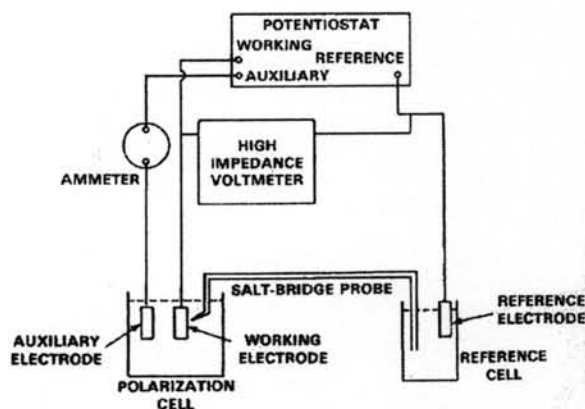

Figure 2.12 Instrumentation set up for potentiodynamic polarization test (Fontana, 1986).
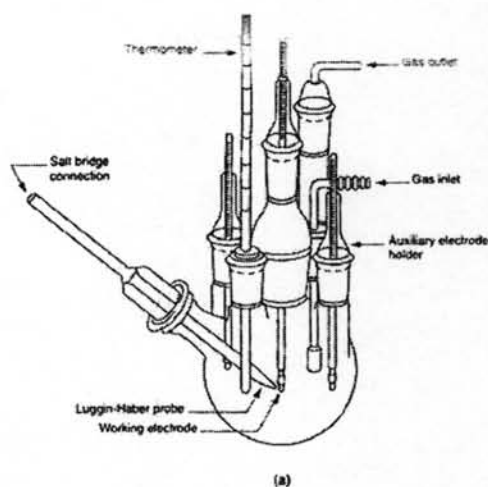
29

(a)

Figure 2.13 Designs of working electrodes (© 1984 EG&G Princeton Applied
Research Inc.) (Fontana, 1986).

2.4.3 Faraday's Law and Corrosion Rate Calculation

The corrosion process involves consuming or producing the electrons,
as the rate of reaction is conveniently measured as current. The proportionality of
current and mass reacted, m, is given by Faraday's Law:

$$m = \frac{Ita}{nF}$$ (2.34)

Where

I	=	Current
F	=	Faraday's constant, 96,500 coulombs/equivalent
n	=	the number of equivalent exchanged electrons
a	=	atomic weight
t	=	time

Corrosion can be expressed in various units, commonly in terms of
mass loss rate and/or penetration rate. Mass loss rate, mass/ (time×area), can be

obtained by dividing the equation (2.34) with time and exposed area.

$$r = \frac{m}{tA} = \frac{ia}{nF} \qquad (2.35)$$

i is defined as a current density, I/A, (current/area exposed).

The term a/n in equation (2.35) is equivalent weight which is the mass of metal in grams that is oxidized by the passage of one Faraday (96,500 coulombs). For an alloy which contains more than one element, the equivalent weight is a weight average of a/n for the major alloying elements in any given alloys as shown in equation (2.36) and the example of calculation is given in Appendix B.

$$EW^{-1} = N_{EQ} = \Sigma\left(\frac{f_i}{a_i / n_i}\right) = \Sigma\left(\frac{f_i n_i}{a_i}\right) \qquad (2.36)$$