

**A STUDY OF CORROSION TO THE CARBON STEEL IN THE PRESENT OF  
CARBON DIOXIDE**

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requirements for the award of the degree of  
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## ABSTRACT

The study describes on effect of several environmental factors of the corrosion rate in the pipeline. Transmission gas pipeline is an important part of oil and gas industries and the carbon steel is a primary material for construction the pipeline due to its low cost and availability, but it is very susceptible to corrosion in CO<sub>2</sub> environments. Carbon dioxide (CO<sub>2</sub>) corrosion is the major problem in oil and gas industries that causes the pipeline failures. Aqueous carbon dioxide (carbonic acid) is corrosive and corrodes the carbon steel pipelines and it is influenced by several environmental factors such as pH, temperature, partial pressure of CO<sub>2</sub>, hydrodynamics, etc. Actually there are many types of corrosion which occur in pipeline but in this study only focused on CO<sub>2</sub> corrosion and only two environmental factors which is pH and temperature were investigated. In this study, SOLTEQ Corrosion Study Kits, Model BP01 is used as an apparatus to examine the corrosion rate of metal. Based on the result from the experiment, it was stated that acidic condition recorded the corrosion rate of weight loss was very high. In the temperature test with 3.5% NaCl solution, corrosion rate was high at temperature 120<sup>0</sup>C. From the research, the corrosion occurred in high temperature condition and at low pH environment. As the temperature increase, the corrosion rate also increases due to the dissolution of iron ion and formation of weak carbonic acid. The weak carbonic acid dissociates into carbonate and hydrogen ion, which increase the cathodic reaction on the metal surface. In acidic condition, the available H<sup>+</sup> ions makes H<sup>+</sup> reduction the dominating cathodic reaction and corrosion rate is found to be sensitive at this low pH.

## ABSTRAK

Kajian ini menjelaskan tentang beberapa factor persekitaran yang mempengaruhi kadar pengaratan dalam paip. Paip penghantaran gas merupakan sebahagian penting dari industri minyak dan gas dan baja karbon merupakan bahan utama untuk pembinaan paip kerana kos yang rendah dan ketersediaan, tetapi ia nya mudah terpengaruh terhadap pengaratan dalam persekitaran karbon dioksida. Pengaratan karbon dioksida merupakan masalah utama dalam industri minyak dan gas yang menyebabkan kegagalan paip. Karbon dioksida berair ( asid karbonik) adalah bersifat menghakis dan menyebabkan paip berkarat dan hal ini dipengaruhi oleh beberapa factor persekitaran seperti pH, suhu, tekanan separa karbon dioksida, hidrodinamika, dan lain-lain. Sebenarnya terdapat banyak jenis hakisan yang berlaku dalam paip tetapi dalam kajian ini hanya difokuskan pada pengaratan karbon dioksida dan hanya dua faktor persekitaran pH dan suhu dikaji. Dalam kajian ini, SOLTEQ Corrosion Study Kit, Model BP01 digunakan sebagai alat untuk menguji kadar pengaratan logam. Berdasarkan eksperimen yang telah dibuat, dinyatakan bahawa keadaan asid mencatat penurunan berat yang paling tinggi. Pada uji suhu dengan larutan NaCl 3.5%, kadar pengaratan adalah paling tinggi berlaku pada suhu 120<sup>0</sup>C. Dari kajian, pengaratan berlaku pada keadaan suhu yang tinggi dan pada pH yang rendah. Sebagai kenaikan suhu, kadar pengaratan juga meningkat akibat pembubaran ion besi dan pembentukan asid karbonat lemah. Asid karbonik lemah tercerai menjadi karbonat dan ion hydrogen yang meningkatkan reaksi katodik pada permukaan logam. Dalam keadaan asid, ion H<sup>+</sup> menyebabkan penurunan H<sup>+</sup> yang mendominasi reaksi katodik dan kadar pengaratan yang tinggi berlaku pada suhu yang rendah.

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## LIST OF SYMBOLS & ABBREVIATIONS

$\text{H}_2\text{CO}_3$	-	Carbonic Acid
$\text{NaOH}$	-	Sodium Hydroxide
$\text{NaCl}$	-	Sodium Chloride
$\text{FeCO}_3$	-	Ferrous Carbonate
$\text{HCl}$	-	Hydrochloric Acid
$\text{H}_2\text{S}$	-	Hydrogen Sulphide
$\text{H}_2\text{O}$	-	Water
$\text{CO}_2$	-	Carbon Dioxide
$\text{OH}^-$	-	Hydroxide ion
$\text{O}_2$	-	Oxygen
$\text{H}_2$	-	Hydrogen
$\text{HCO}_3^-$	-	Bicarbonate ion
$\text{CO}_3^{2-}$	-	Carbonate ion
$\text{Fe}^{2+}$	-	Iron ion
$\text{H}^+$	-	Hydrogen ion
$\text{Mn}$	-	Manganese
$\text{Al}$	-	Aluminium
$\text{P}$	-	Phosphorus
$\text{S}$	-	Sulphur
$e^-$	-	Electron
aq	-	Aqueous
l	-	Liquid
g	-	Gas



## LIST OF APPENDICES

- Appendix A - Calculation rate of corrosion for pH effect
- Appendix B - Calculation rate of corrosion for temperature effect



## CHAPTER 4

### RESULT & DISCUSSION

#### 4.1 Result

Three sets of experiments were conducted at pH 4, 7 and 9 with the temperature was constant at room temperature and also four sets of experiments were conducted at temperatures 30<sup>0</sup>C, 60<sup>0</sup>C, 90<sup>0</sup>C and 120<sup>0</sup>C in 3.5wt% of NaCl salt solution. The corrosion rates were calculated and Table 4.1 and Table 4.2 shown the calculated rate of corrosion for both effect of pH and temperature.

##### 4.1.1 Effect of pH

pH	Rate of Corrosion (g/day)		
	TRIAL 1	TRIAL 2	TRIAL 3
4	0.02619	0.01905	0.01667
7	0.09238	0.05286	0.03952
9	0.03095	0.02952	0.02619

Table 4.1 Rate of corrosion of steel at different pH

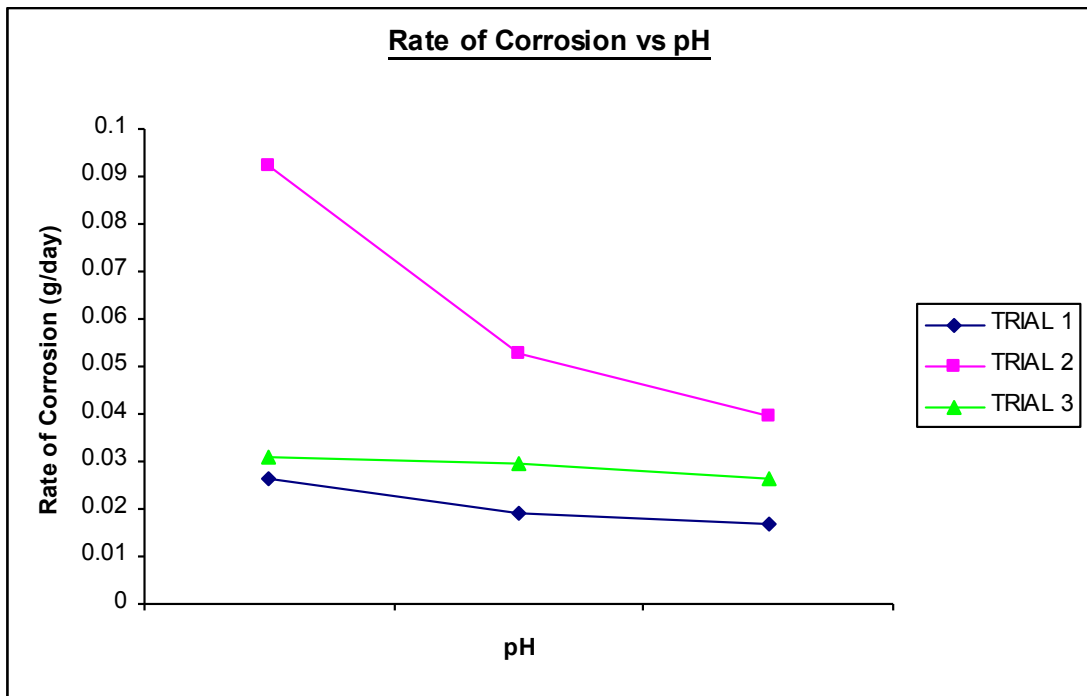


Figure 4.1 Graph of pH versus Rate of Corrosion

The effect of pH on corrosion rate was studied in three different pH which was 4, 7 and 9 at room temperature. The experiments were conducted with three trials to get more accurate results. From the graph of pH versus rate of corrosion above for the trial 1, corrosion rates decreased from 0.02619 g/day to 0.01667 g/day with the increased of pH. For the trial 2, corrosion rate decreased from 0.09238 g/day to 0.03952 g/day and for the trial 3, corrosion rate decreased from 0.03095 g/day to 0.02619 g/day.

#### 4.1.2 Effect of Temperature

Temperature (°C)	Rate of Corrosion (g/hr)
30	0.00028
60	0.00035
90	0.00049
120	0.00118

Table 4.2 Rate of corrosion of steel at different temperature

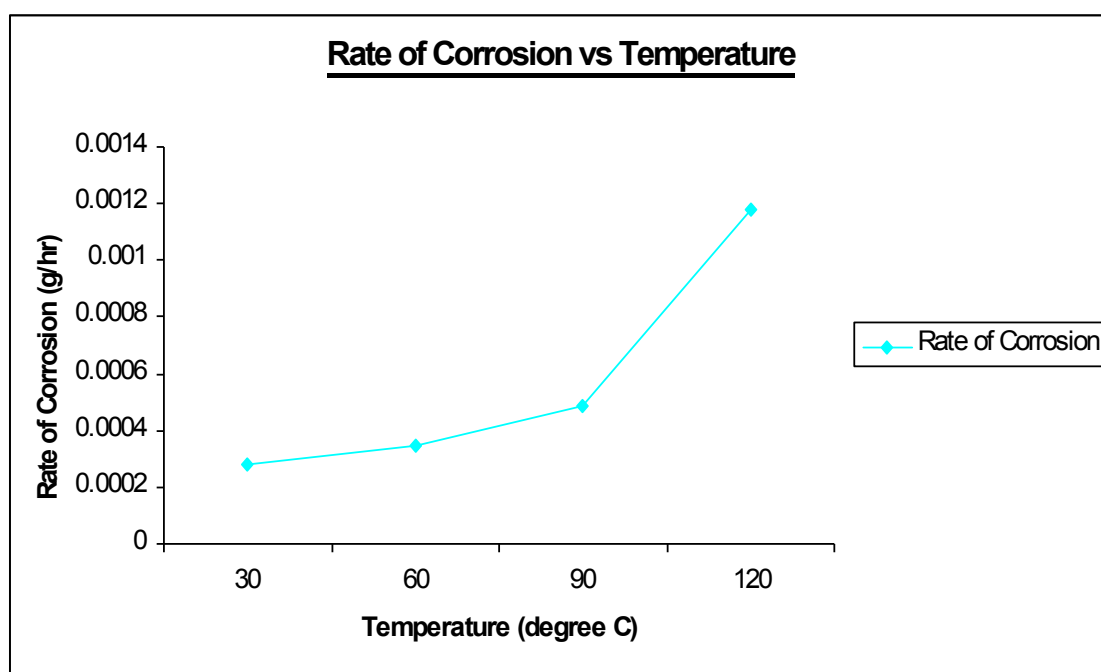


Figure 4.2 Graph of Temperature versus Rate of Corrosion

Table 2 above shown the result of the effect of temperature on the rate of corrosion of steel. Figure shown the corrosion rates of steel under the condition of different temperature 30°C, 60°C, 90°C and 120°C in 3.5wt% NaCl salt solution. General CO<sub>2</sub> rates changed from 0.00028 g/hr at 30°C to 0.00118 g/hr at 120°C.

## 4.2 Discussion

The pH represents the hydrogen ion concentration in a given solution. Changing pH has a very strong effect on localized corrosion and general corrosion. From the results of pH, corrosion rate decreased with an increased of pH, because the concentration of one of the key corrosion species, hydrogen ion ( $H^+$ ) decreased with the increased of pH. From the figure also shown that corrosion rate higher in acidic condition. Under this condition, the reduction potential of  $H^+$  is higher than the oxidation potential of the iron pipe. At a pH lower than 4, the proton reduction is the dominated cathodic reaction, while at a pH higher than 4, the dominated reaction is the reduction of carbonic acid.

Difference with temperature, when the increase of temperature introduce the higher corrosion rate it will be. At low temperature, corrosion rate of samples slowly increased due to the continuous dissolution of  $Fe^{2+}$  ion in the solution as a result of formation of porous  $FeCO_3$ . Temperature is known to accelerate most of the chemical and electrochemical processes occurring in the present system. The high temperature accelerated dissolution of pipe wall, with an increased in availability of  $Fe^{2+}$  ions for used in the  $FeCO_3$  precipitation reaction. Because the high temperature also reduced the solubility of  $FeCO_3$ , this increased in corrosion rate is balanced by the formation of a continuous, tightly adherent film of ferrous carbonate which will inhibit further corrosion.

## CHAPTER 1

### INTRODUCTION

#### 1.1 Background of study

Transmission gas pipelines are an important part of national energy-transportation infrastructure vital to the national economy. The pipelines are operated at high pressure and when pipeline failure occur, it can cause severe damage to human health and property and interruption of gas supplies (Glenn M. Light et al., Sept 2003). But the most common problem that oil and gas industries facing today is a corrosion in pipeline. Compounds such as carbon dioxide, water and hydrogen sulphide are present naturally in gas wells. Carbon dioxide which is present naturally is also injected purposely into gas wells to enhance oil recovery. These compounds combine to form a corrosive environment under different environmental conditions such as temperature, pressure, pH and concentration (Venkatasubramaniyan Sridharan, June 2009).

Corrosion is the unwanted and undesired loss of material (metal) due to the reaction of the material (metal) with its surrounding or environment. Corrosion is the most common problem that causes pipeline failures that used in the extraction, production and transportation of oil and gas in the petroleum industries. A typical type of

corrosion is carbon dioxide ( $\text{CO}_2$ ) corrosion, also known as "sweet corrosion", is one of the major problems in oil and gas industry, costing billions of dollars every year which involves the presence of carbon dioxide ( $\text{CO}_2$ ) (NACE, 15 April 2009). In  $\text{CO}_2$  corrosion,  $\text{CO}_2$  dissolves and hydrates to form carbonic acid ( $\text{H}_2\text{CO}_3$ ), which then dissociates into bicarbonate, carbonate and hydrogen ions. Carbon steel is used as the primary construction material for pipelines in oil and gas industries due to its low cost and availability, but it is very susceptible to corrosion in  $\text{CO}_2$  environments. Aqueous carbon dioxide (carbonic acid) is corrosive and corrodes the carbon steel pipelines. Carbon dioxide corrosion has been of interest to researchers in oil industries for many years and there exists many theories about the mechanism of  $\text{CO}_2$  corrosion (Venkatasubramaniyan Sridharan, June 2009).

Unprotected pipelines, whether buried in the ground, exposed to the atmosphere, or submerged in water, are susceptible to corrosion. Without proper maintenance, every pipeline system will eventually deteriorate. Corrosion can weaken the structural integrity of a pipeline and make it an unsafe vehicle for transporting potentially hazardous materials. The CONCAWE Oil Pipelines Management Group's Special Task Force (Davis et al., 2000) reported that there have been eleven incidents that resulted in a gross spillage total of  $516\text{m}^3$  in Western Europe in 1999. A total of a quarter of the accidents was caused by corrosion and resulting in a total spillage of  $199\text{m}^3$  of hydrocarbon products.

## 1.2 Problem statement

Carbon dioxide system are one of the common environments in the pipeline steel and process equipments used in the extraction, production and transportation of oil and gas in the petroleum industry where corrosion occurs. The corrosion in pipeline are

influenced by many parameters such as pH, temperature, pressure and surface films (C. de Waard et al., 1975). There are many effects of pipeline failures due to the corrosion such as loss of metal, pressure drop will occur in pipeline, cracking and also may constitute serious hazards to the gas in the pipeline. Besides that, corrosion also may damage the pipeline and can cause the leakage that may hazards to the environment, assets and even humans (Malaysian Journal of Civil Engineering 21(1): 69 -81(2009)). In this study, the parameters that influence the rate of corrosion in pipeline occurs which are temperature and pH are the main objectives to examine.

### 1.3 Objectives

The purpose of this study is to examine the effect of pH and temperature on the rate of corrosion of steel

### 1.4 Scope of study

To achieve the objectives, several scopes have been identified in this study. The scopes of this study are:-

- i. To determine the pH where the corrosion occurs
- ii. To study the effect of temperature on corrosion
- iii. To determine which will be the good condition for less corrode condition for carbon steel.



## 1.5 Significance of study

The study of corrosion in pipeline in the presence of carbon dioxide is beneficial to the oil and gas industries. There are several benefits which are:

- i. Preventing the corrosion in pipeline system.
- ii. Reduce the cost needed for maintenances of pipeline failures.
- iii. Give information about what the condition that corrosion can occur.



## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Introduction

The economics of oil and gas production are complicated endeavor. One of the major decisions made before a well is drilled is the material of construction for the pipeline and this is depends on the lifetime of the well (Keith s.George,2003). Carbon steels are generally used for the petroleum industry for transportation of crude oils and gasses from offshore to different refining platform and to different destination of the applications (G. S. Das et al.,2004). This is because carbon steel is available in most countries, easy to weld or install, and less expensive than corrosion resistant alloys. On the other hand, carbon steel corrodes in the multiphase (oil/water/gas) mixtures it transports and it depends on several parameters such as partial pressure of CO<sub>2</sub>, temperature, pH and etc. In this study focused on some of the parameters that effect the corrosion in pipeline which is pH and temperature.

During the initial production from a well, the multiphase mixture contains mostly oil and a gas phase consisting of hydrocarbons, carbon dioxide and nitrogen naturally. Brine can also be present in small amount produced increases as the well ages. Dissolved

in the oil is a mixture of organic compounds, which can include paraffins, waxes, and organic acids (Keiths. George,2003). The presence of organic acids compound in oil and gas lines was first discovered in 1994 (Crolet,1999).

Corrosion is recognized as one of the most dominant forms of deterioration process and as one of the major causes for loss of containment in pipelines (Papadakis, 1999).Corrosion in pipeline is an electrochemical and chemical reaction. The types of corrosion in offshore pipelines depend on the nature of hydrocarbon wells of either sweet or sour corrosion (Malaysian Journal of Civil Engineering 21(1) : 69 - 81(2009)). There are many types of internal corrosion of pipeline (William C. Lyons et al);

- i. 'sweet' corrosion , caused by  $\text{CO}_2$  or organic acids plus water
- ii. 'sour' corrosion due to the presence of  $\text{H}_2\text{S}$  and water
- iii. Oxygen corrosion, caused by the interaction of  $\text{O}_2$  and water

## 2.2 Basic of Corrosion

Corrosion is an electrochemical reaction composed of two half cell reactions, an anodic reaction and a cathodic reaction. The anodic reaction releases electrons, while the cathodic reaction consumes electrons. There are three common cathodic reactions, oxygen reduction (fast), hydrogen evolution from neutral water (slow), and hydrogen evolution from acid (fast) (NM WAIDS Corrosion Theory).

### 2.2.1 The corrosion cell

The corrosion cell can be represented as follows:

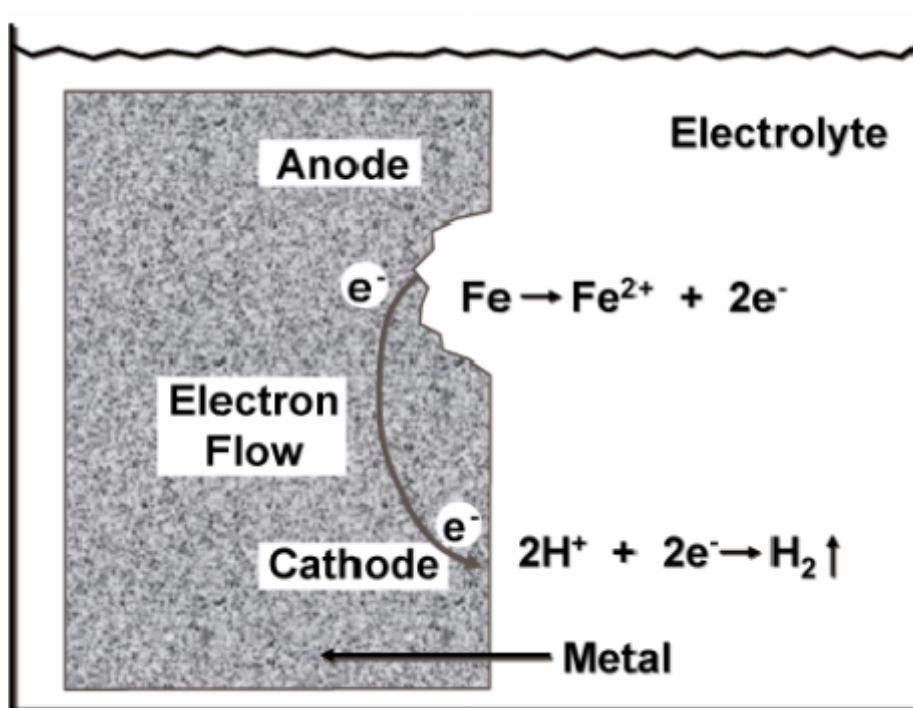


Figure 2.1 The basic corrosion cell

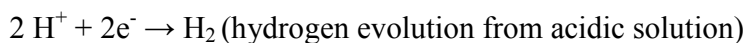
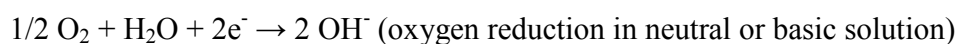
Anodic reaction:



*M stands for a metal and n stands for the number of electrons that an atom of the metal will easily release.*

i.e. for iron and steel:  $Fe \rightarrow Fe^{2+} + 2e^{-}$

Cathodic reactions:



Each half-cell reaction has an electrical potential, known as the half-cell electrode potential. The anodic reaction potential,  $E_a$ , plus the cathodic reaction potential,  $E_c$ , adds

up to  $E$ , the cell potential. If the overall cell potential is positive, the reaction will proceed spontaneously (NM WAIDS Corrosion Theory).

Every metal or alloy has a unique corrosion potential in a defined environment. When the reactants and products are at an arbitrarily defined standard state, the half-cell electrode potentials are designated  $E^\circ$ . These standard potentials are measured with respect to the standard hydrogen electrode (SHE). A listing of standard half-cell electrode potentials is given in Table 2.1.

Selected half-cell reduction potentials are given in Table 2.1. To determine oxidation potentials, reverse the direction of the arrow and reverse the sign of the standard potential. For a given cathodic reaction, those anodic (reversed) reactions below it in the table will go spontaneously, while those above it will not. Thus any metal below the hydrogen evolution reaction will corrode (oxidize) in acidic solutions.

e.g.,

Cathodic reaction:  $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$  (hydrogen evolution)

Two possible anodic reactions:

$\text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{e}^-$  (above cathodic rxn in table - will not corrode)

$\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$  (below cathodic rxn in table - spontaneous corrosion)

Thus, in the presence of  $\text{H}^+$  ions, Zinc (Zn) will spontaneously corrode while copper (Cu) will not.

**Table 2.1 Standard Electromotive Force Potentials**

Cathodic Reactions	Standard Potential, $e^{\circ}$ (volts vs. SHE)
$\text{Au}^{3+} + 3e^{-} \rightarrow \text{Au}$	+1.498 ( <b>Most Noble</b> )
$\text{O}_2 + 4\text{H}^{+} + 4e^{-} \rightarrow 2\text{H}_2\text{O}$	+1.229 (in acidic solution)
$\text{Pt}^{2+} + 2e^{-} \rightarrow \text{Pt}$	+1.118
$\text{NO}_3^{-} + 4\text{H}^{+} + 3e^{-} \rightarrow \text{NO} + 2\text{H}_2\text{O}$	+0.957
$\text{Ag}^{+} + e^{-} \rightarrow \text{Ag}$	+0.799
$\text{O}_2 + 2\text{H}_2\text{O} + 4e^{-} \rightarrow 4\text{OH}^{-}$	+0.401 (in neutral or basic solution)
<b><math>\text{Cu}^{2+} + 2e^{-} \rightarrow \text{Cu}</math></b>	<b>+0.337</b>
<b><math>2\text{H}^{+} + 2e^{-} \rightarrow \text{H}_2</math></b>	<b>0.000</b>
$\text{Pb}^{2+} + 2e^{-} \rightarrow \text{Pb}$	-0.126
$\text{Sn}^{2+} + 2e^{-} \rightarrow \text{Sn}$	-0.138
$\text{Ni}^{2+} + 2e^{-} \rightarrow \text{Ni}$	-0.250
$\text{Co}^{2+} + 2e^{-} \rightarrow \text{Co}$	-0.277
$\text{Cd}^{2+} + 2e^{-} \rightarrow \text{Cd}$	-0.403
$\text{Fe}^{2+} + 2e^{-} \rightarrow \text{Fe}$	-0.447
$\text{Cr}^{3+} + 3e^{-} \rightarrow \text{Cr}$	-0.744
<b><math>\text{Zn}^{2+} + 2e^{-} \rightarrow \text{Zn}</math></b>	<b>-0.762</b>
$2\text{H}_2\text{O} + 2e^{-} \rightarrow \text{H}_2 + 2\text{OH}^{-}$	-0.828 (pH = 14)
$\text{Al}^{3+} + 3e^{-} \rightarrow \text{Al}$	-1.662
$\text{Mg}^{2+} + 2e^{-} \rightarrow \text{Mg}$	-2.372
$\text{Na}^{+} + e^{-} \rightarrow \text{Na}$	-2.71
$\text{K}^{+} + e^{-} \rightarrow \text{K}$	-2.931 ( <b>Most Active</b> )

Source: Handbook of Chemistry and Physics, 71st ed, CRC Press, 1991

Table 1 can be used to show that copper will corrode in nitric acid solutions (oxidizing) and aerated water. Similarly, aluminum (Al), magnesium (Mg), sodium (Na) and potassium (K) will react spontaneously with water in neutral or basic solutions (NM WAIDS Corrosion Theory).

### 2.3 CO<sub>2</sub> Corrosion

In this study, we only focus on the CO<sub>2</sub> corrosion. CO<sub>2</sub> corrosion, which also called “sweet corrosion”, is the common problem in oil and gas industries. It can cause pipeline failures and the mechanism of CO<sub>2</sub> corrosion has been studied over the past few decades. The researchers have already identified several environmental factors that effect the corrosion in pipeline such as CO<sub>2</sub> partial pressure, pH, temperature, hydrodynamics, etc. The research about the CO<sub>2</sub> corrosion have been made by de Waard et al in 70’s and 80’s by Dugstad et al and Grey et al in the 90’s, and Nescic’s group over the past 10-15 years (Shufan Wang, March 2009).

### 2.3.1 CO<sub>2</sub> Corrosion Mechanism

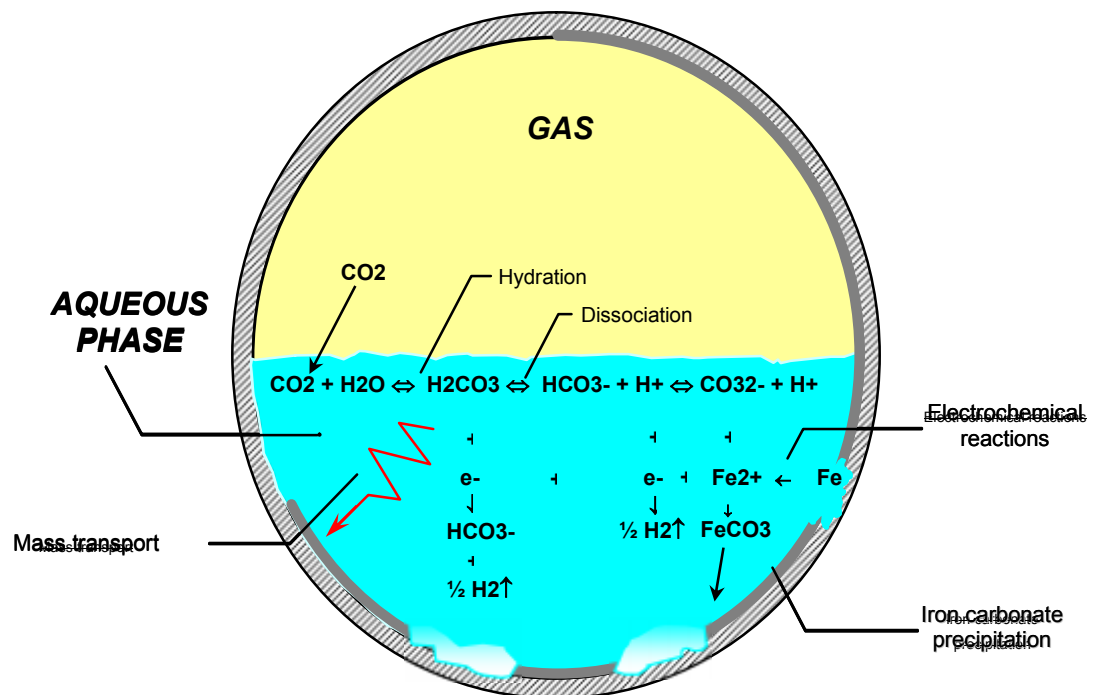


Figure 2.2 CO<sub>2</sub> Corrosion Mechanisms (Corrosion Awareness Training, PCSB Myanmar Operation)

The following reactions describe what happens during the CO<sub>2</sub> corrosion process (Venkatasubramaniyan Sridhan, June 2009). First the gas phase carbon dioxide dissolves in the water and undergoes hydration to form carbonic acid:



Carbonic acid then dissociates into bicarbonate and carbonate ions in two cathodic steps. The cathodic reaction also includes reduction of hydrogen ions:

Carbonic acid reduction:



Proton reduction:



The cathodic reduction involves two reactions depending on the pH. At pH lower than 4, the proton reduction is dominant cathodic reaction, while at a pH higher than 4, the dominant reaction is the reduction of carbonic acid (Venkatasubramaniyan Sridhan, June 2009). The CO<sub>2</sub> corrosion reaction includes the anodic dissolution of iron at the metal surface and given by:

