

MECHANISTIC STUDY OF CO<sub>2</sub> CORROSION RELATED TO CORROSION IN OIL  
AND GAS EXPLORATION AND PRODUCTION

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## ABSTRACT

A mechanistic model of CO<sub>2</sub> corrosion in the presence of H<sub>2</sub>S has been developed. A model has been developed for the computation of corrosion rates of carbon steels in presence of carbon dioxide and hydrogen sulfide. The model included an electrochemical model for partial cathodic and anodic process on the metal surface. The partial processes taken into account by the model include the oxidation of iron and reduction of hydrogen ions, water, carbonic acid and hydrogen sulfide. The model has been verified by comparing calculated corrosion rates with corrosion model prediction software. The corrosion model prediction software consists of Freecorp, Norsok, Cassandra and ECE. The effects of various conditions such as temperature and pH value on corrosion rates has been analyze. The trends shown in the predictions agreed well with the general understanding of the CO<sub>2</sub> corrosion process in the presence of H<sub>2</sub>S.

## ABSTRAK

Satu model mekanistik kakisan  $\text{CO}_2$  dengan kehadiran  $\text{H}_2\text{S}$  telah dibangunkan. Model telah dibangunkan untuk pengiraan kadar kakisan keluli karbon dengan kehadiran karbon dioksida dan hidrogen sulfida. Model ini termasuk model untuk proses elektrokimia katod dan anodic separa pada permukaan logam. Proses separa diambil kira oleh model ini termasuk pengoksidaan besi dan pengurangan ion hidrogen, air, asid karbonik dan hidrogen sulfida. Model ini telah disahkan dengan membandingkan kadar hakisan model dengan kakisan model perisian ramalan. Model hakisan perisian ramalan terdiri daripada Freecorp, Norsok, Cassandra dan ECE. Kesan daripada pelbagai keadaan seperti suhu dan nilai pH pada kadar hakisan telah dianalisis. Trend yang ditunjukkan dalam model ramalan sama juga dengan pemahaman umum proses hakisan  $\text{CO}_2$  dengan  $\text{H}_2\text{S}$ .

## TABLE OF CONTENT

|                                     |  | <b>Page</b> |
|-------------------------------------|--|-------------|
| <b>EXAMINER'S APPROVAL DOCUMENT</b> |  | ii          |
| <b>SUPERVISOR'S DECLARATION</b>     |  | iii         |
| <b>STUDENT'S DECLARATION</b>        |  | iv          |
| <b>ACKNOWLEDGEMENTS</b>             |  | v           |
| <b>ABSTRACT</b>                     |  | vi          |
| <b>ABSTRAK</b>                      |  | vii         |
| <b>TABLE OF CONTENTS</b>            |  | viii        |
| <b>LIST OF TABLE</b>                |  | xi          |
| <b>LIST OF FIGURE</b>               |  | xii         |
| <b>LIST OF ABBREVIATIONS</b>        |  | xiv         |
|                                     |  |             |
| <b>CHAPTER 1</b>                    | <b>INTRODUCTION</b>  |             |
|                                     |  |             |
| 1.1                                 | Background   | 1           |
| 1.2                                 | Problem Statement  | 2           |
| 1.3                                 | Research Objective   | 2           |
| 1.4                                 | Scope Of Study   | 3           |
|                                     |  |             |
| <b>CHAPTER 2</b>                    | <b>LITERATURE REVIEW</b>   |             |
|                                     |  |             |
| 2.1                                 | CO <sub>2</sub> Corrosion  | 4           |
| 2.2                                 | Basic Corrosion Kinetics   | 5           |
|                                     | 2.2.1 Anode Reaction   | 6           |
|                                     | 2.2.2 Cathode Reaction   | 6           |
|                                     | 2.2.2.1 Hydrogen ion reduction                                   | 6           |
|                                     | 2.2.2.2 Hydrogen ions produced by reduction<br>reaction of water | 7           |
|                                     | 2.2.2.3 Reduction of carbonic acid                               | 8           |

|   |  |    |
|---|--|----|
| 2.3   | The Effect of pH   | 9  |
| 2.4   | The Effect of Temperature  | 9  |
| 2.5   | Corrosion Product Film Formation   | 10 |
|   | 2.5.1 Iron carbide ( $\text{Fe}_3\text{C}$ )                             | 10 |
|   | 2.5.2 Iron carbonate ( $\text{FeCO}_3$ )                                 | 10 |
|   | 2.5.3 Iron sulfide ( $\text{FeS}$ )                                      | 11 |
| 2.6   | The Effect of $\text{H}_2\text{S}$                                       | 12 |
| 2.7   | $\text{CO}_2$ Corrosion Model  | 14 |
|   | 2.7.1 De Waard Model   | 14 |
|   | 2.7.2 Norsok M-506 Model   | 14 |
|   | 2.7.3 Cassandra Model  | 15 |
|   | 2.4.4 ECE Model  | 15 |
| 2.8   | Effect $\text{H}_2\text{S}$ on $\text{CO}_2$ Corrosion                   | 16 |
| <br>  |  |    |
| <b>CHAPTER 3      METHODOLOGY</b>           |  |    |
| <br>  |  |    |
| 3.1   | Introduction   | 17 |
| 3.2   | Flow Chart   | 18 |
| 3.3   | Design Corrosion Model   | 19 |
| 3.4   | Verification   | 19 |
| 3.5   | Calculating Test Accuracy  | 19 |
|   | 3.5.1 Model validation   | 20 |
| <br>  |  |    |
| <b>CHAPTER 4      RESULT AND DISCUSSION</b> |  |    |
| <br>  |  |    |
| 4.1   | Introduction   | 22 |
| 4.2   | $\text{CO}_2$ Corrosion Model  | 23 |
| 4.3   | Effect of Temperature on Corrosion Rate in $\text{CO}_2$ Corrosion Model | 25 |
| 4.4   | Effect of pH Value on Corrosion Rate in $\text{CO}_2$ Corrosion Model    | 26 |

|  |   |    |
|--|---|----|
| 4.5  | Effect of H <sub>2</sub> S in Combination with pH and Temperature in CO <sub>2</sub> Corrosion Model                          | 28 |
| 4.6  | Verification for the Corrosion Model with Corrosion Prediction Software   | 29 |
| 4.6.1  | Comparison between Corrosion Models and Corrosion Prediction Software for Different Temperature                               | 30 |
| 4.6.2  | Comparison between Corrosion Models and Corrosion Prediction Software for Different pH value                                  | 35 |
| 4.7  | Verification for the Corrosion Model in Presence of H <sub>2</sub> S with Corrosion Prediction Software                       | 38 |
| 4.7.1  | Comparison between Corrosion Models in Presence of H <sub>2</sub> S and Corrosion Prediction Software with pH and Temperature | 38 |
| <b>CHAPTER 5 CONCLUSION AND RECOMMENDATION</b> |   |    |
| 5.1  | Introduction  | 41 |
| 5.2  | Conclusion  | 41 |
| 5.3  | Recommendation  | 42 |
| <b>REFERENCES</b>                              |   | 43 |

**LIST OF TABLE**

| <b>Table No.</b> |  | <b>Page</b> |
|------------------|--|-------------|
| 4.1              | Corrosion rates of the model at various temperature                        | 25          |
| 4.2              | Corrosion rates of the model at various pH values                          | 27          |
| 4.3              | Corrosion rates of the model at various concentrations of H <sub>2</sub> S | 28          |
| 4.4              | Comparisons between corrosion model and Norsok software                    | 30          |
| 4.5              | Comparisons between corrosion model and Freecorp software                  | 32          |
| 4.6              | Relationships between corrosion model and ECE software                     | 33          |
| 4.7              | Relationships between corrosion model and cassandra software               | 34          |
| 4.8              | Comparisons between corrosion model and Norsok software                    | 35          |
| 4.9              | Comparisons between corrosion model and cassandra software                 | 37          |
| 4.10             | Comparisons between corrosion model and Freecorp software                  | 39          |
| 4.11             | Comparisons between corrosion model and ECE software                       | 40          |

## LIST OF FIGURE

| <b>Figure No.</b> |   | <b>Page</b> |
|-------------------|---|-------------|
| 2.1               | Corrosion regimes in CO <sub>2</sub> /H <sub>2</sub> S corrosion defined by Posts, et al  | 13          |
| 3.1               | Flow Chart  | 18          |
| 4.1               | CO <sub>2</sub> corrosion model for different temperature at pressure of CO <sub>2</sub> 1 bar, pH value 4  | 23          |
| 4.2               | CO <sub>2</sub> corrosion model for different pH value at pressure of CO <sub>2</sub> 1 bar, temperature 25 <sup>0</sup> C  | 24          |
| 4.3               | CO <sub>2</sub> corrosion model for different PPM at pressure of CO <sub>2</sub> 1 bar, temperature 25 <sup>0</sup> C, pH value 4 in presence of H <sub>2</sub> S               | 24          |
| 4.4               | Relationships between corrosion rates of the model at various temperatures at pressure of CO <sub>2</sub> 1bar, pH value 4 and without presence of H <sub>2</sub> S             | 26          |
| 4.5               | Relationships between corrosion rates of the model at various pH values at pressure of CO <sub>2</sub> 1bar, pH value 4 and without presence of H <sub>2</sub> S                | 27          |
| 4.6               | Relationships between corrosion rates of the model at various concentrations of H <sub>2</sub> S at pressure of CO <sub>2</sub> 1bar, temperature 23 <sup>0</sup> C, pH value 4 | 29          |
| 4.7               | Comparisons between corrosion model and Norsok software at pH4, pressure CO <sub>2</sub> 1bar and 0ppm of H <sub>2</sub> S  | 31          |
| 4.8               | Comparisons between corrosion model and Freecorp software at pH4, pressure CO <sub>2</sub> 1bar and 0ppm of H <sub>2</sub> S  | 32          |



|      |   |    |
|------|---|----|
| 4.9  | Relationships between corrosion model and ECE software at pH4, pressure CO <sub>2</sub> 1bar and 0ppm of H <sub>2</sub> S                               | 33 |
| 4.10 | Relationships between corrosion model and Freecorp software at pH4, pressure CO <sub>2</sub> 1bar and 0ppm of H <sub>2</sub> S                          | 34 |
| 4.11 | Comparisons between corrosion model and Norsok software at temperature 25 <sup>0</sup> C, pressure CO <sub>2</sub> 1bar and 0ppm of H <sub>2</sub> S    | 36 |
| 4.12 | Comparisons between corrosion model and Cassandra software at temperature 25 <sup>0</sup> C, pressure CO <sub>2</sub> 1bar and 0ppm of H <sub>2</sub> S | 37 |
| 4.13 | Comparisons between corrosion model and Freecorp software at temperature 25 <sup>0</sup> C, pressure CO <sub>2</sub> 1bar and pH 4                      | 39 |
| 4.14 | Comparisons between corrosion model and ECE software at temperature 25 <sup>0</sup> C, pressure CO <sub>2</sub> 1bar and pH 4                           | 40 |

**LIST OF ABBREVIATIONS**

|                         |                               |
|-------------------------|-------------------------------|
| $\text{CO}_2$           | Non Revenue-Water             |
| $\text{H}_2\text{S}$    | Asbestos Cement               |
| ECE                     | Electronic Corrosion Engineer |
| g                       | Gas Phase                     |
| aq                      | Aqueous Phase                 |
| $\text{H}_2\text{O}$    | Water                         |
| $\text{H}_2\text{CO}_3$ | Carbonic Acid                 |
| Fe                      | Iron                          |
| $\text{O}_2$            | Oxygen                        |
| $i$                     | Current Density               |
| R                       | Universal Gas Constant        |
| F                       | Faraday Constant              |
| $b$                     | Tafel Slope                   |
| a                       | Concentration                 |
| $i_a$                   | Activation Reaction Current   |
| $i_{lim}$               | Limiting Diffusion Current    |
| T                       | Temperature                   |
| $K_m$                   | Mass Flow Coefficient         |
| $\text{H}_2$            | Hydrogen                      |
| $\text{Fe}_3\text{C}$   | Iron Carbide                  |

|                   |                  |
|-------------------|------------------|
| FeCO <sub>3</sub> | Iron Carbonate   |
| FeS               | Iron Sulfide     |
| S                 | Supersaturation  |
| PPM               | Part per Million |
| DW                | De Waard         |
| HAc               | Acetic Acid      |

## **CHAPTER 1**

### **INTRODUCTION**

#### **1.1 BACKGROUND**

Carbon dioxide corrosion can be defined as the attack of metal by aqueous CO<sub>2</sub> environments. Carbon dioxide corrosion also can be called as sweet corrosion. The CO<sub>2</sub> corrosion is a significant problem in oil and gas environment. In the liquid phase, the gas can be dissolved in water produces carbonic acid which is active against steel. CO<sub>2</sub> can affect material made of carbon steel with a variety of ways. Mixture elements contains in the oil usually carbon dioxide, hydrogen sulfide and aqueous brine (Anderko & Young, 1999). This component can change the corrosion mechanism of carbon steel. The objective is to study the electro-chemical reactions occurring during the corrosion process (G.Keith, 2004).

CO<sub>2</sub> corrosion prediction model have been developed in many ways. CO<sub>2</sub> corrosion model can be divided into three categories that are empirical models, mechanistic models and semi empirical models. Few models had recently based on empirical corrosion of the processes underlying CO<sub>2</sub> corrosion. It was made several studies in that empirical which occurred in carbon steel related to CO<sub>2</sub> corrosion. In corrosion process involve electrochemistry, chemical process and time transfer processes.

There are various models have been developed by oil companies and research institutions for CO<sub>2</sub> corrosion of carbon steel. Results obtained for the different models used for the same cases will be different. The results obtained are different due to different calculated ways (Nyborg, 2010). The differences in assuming corrosion product film will

determine corrosion rate production. Next, it is difficult to conduct experiment due to the high pressure and high temperature. Thus, it should be important to develop new method to predict corrosion rate.

## **1.2 PROBLEM STATEMENT**

Actual situation influence  $\text{CO}_2$  brings difficulty in experimental and simulation to predict rate of corrosion based on empirical method. There is limited prediction model corrosion in literature quantify mixed variables simultaneously and there is no expression developed previously to display corrosion model in  $\text{CO}_2/\text{H}_2\text{S}$  mechanistically environment.

Modeling mechanistic and simulation need to be done because extreme condition in actual situation make difficult to simulate in laboratory experiment. Therefore, it is important to develop corrosion  $\text{CO}_2$  models that supported by whether strong fundamental theory or proven background analysis that can express relationship among the operational conditions (temperature and pH) and species reservoir ( $\text{H}_2\text{S}$ )

## **1.3 RESEARCH OBJECTIVES**

The main objective of this research is to improve a better understanding of the effect of  $\text{H}_2\text{S}$  on corrosion in  $\text{CO}_2$  environment. The work will be carried out to meet the following specific objectives:

- i. Study  $\text{CO}_2$  corrosion in the presence of  $\text{H}_2\text{S}$  based on mechanistic theories.
- ii. Determine the partial cathodic and anodic processes experienced by  $\text{CO}_2$  corrosion according to the mechanisms determined in the literature.
- iii. Investigate the effects of  $\text{H}_2\text{S}$  in combination with pH and temperature in  $\text{CO}_2$  corrosion.

## 1.4 SCOPE OF STUDY

The research will investigate corrosion rate in CO<sub>2</sub> artificial environmental containing H<sub>2</sub>S in several pH and temperature mechanistically. Discussion of various parameters in the model related to the corrosion mechanism will be based on the available published experimental data and industrial corrosion software. The scopes of this project are:

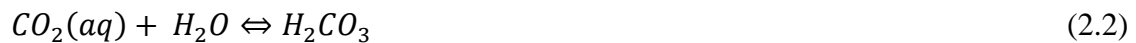
- i. Develop the corrosion model mechanistically.
- ii. Verification with experimental method that have been done by others researcher.
- iii. Simulations using industrial corrosion model software's that are Freecorp, Cassandra and ECE.
- iv. Compared the results obtained between corrosion model with the experimental method and industrial corrosion software.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 CO<sub>2</sub> CORROSION

Carbon dioxide corrosion is a main problem in oil industry and gas. The existence of dry CO<sub>2</sub> gas or the only oil is itself not corrosive. When aqueous phase contact with metal surface it leading to corrode and failures next. CO<sub>2</sub> corrosion is basic reaction was well understood and accepted throughout all over work done in a past few decades (Nordsveen & Netic, 2003). Reaction special chemical include CO<sub>2</sub> dissolution and hydration to form carbonic acid,



It then dissociates into bicarbonate and carbonate ions in two steps:



CO<sub>2</sub> corrosion is an electrochemical reaction with the overall reaction given by:



So, corrosion  $\text{CO}_2$  brings to formation of product corrosion,  $\text{FeCO}_3$ , that when is precipitated can form one protection or a non-protection scale depending at environmental circumstance. Electrochemistry reactions in surface steel include iron anode dissolution:



## 2.2 BASIC CORROSION KINETICS

A corrosion reaction is one anodic dissolution reaction of metal and one cathodic reduction reaction of oxidant. Then both reactions involve the transport process, a typical corrosion process can be divided into three basic steps (Wang, 1997):

1. Transport of oxidants (e.g.  $\text{O}_2$ ,  $\text{H}^+$ ) from bulk solution to metal/solution interface.
2. Surface electrochemical reactions during which the metal corrodes and dissolves into solution and oxidants are reduced on the corroding surface.
3. Transport of dissolved corrosion product and from metal/solution interface to bulk solution.

The corrosion rate can be affected by any one of the steps. The first step and the third step are affected by the mass transfer rate of the oxidants. Iron with an incomplete d-shell and a low value of  $k_s$ , and consequently  $i_o$  was chosen as a representative of metals, whose anodic dissolution is not affected by flow in the absence of film formation (Wang, 1997). Oxygen, hydrogen ion and water reduction are the cathodic reactions considered.



### 2.2.1 Anode Reaction

At the anode reaction occur dissolving metal ions into solution as a reaction to assume controlled by the activation reaction (chemical reaction). As modeled by Bocris that the anode reaction is influenced by the activity of ion  $\text{OH}^-$  Based Mechanism proposed by Bocris, *etc.* Tafel slope for this reaction is worth 40mV/decade. For reversible potential value obtained a value of -0488 V(G.Keith, 2004). Based on these assumptions the equation obtained activation corrosion reaction as follows:

$$i_{(Fe)} = i_{o,(Fe)} \times 10^{\frac{\eta}{b_a}} \quad (2.7)$$

$$i_{(Fe)} = i_{Fe}^o \exp \left[ \frac{-\alpha_{Fe} F (E - E_{Fe}^o)}{RT} \right] \quad (2.8)$$

$$i_{Fe}^o = i_{Fe}^* a_{OH} a_{H_2O}^{1.6} \quad (2.9)$$

### 2.2.2 Cathode Reaction

Cathode reaction occurring in the gas  $\text{CO}_2$  is a composite of some species undergo reduction reaction. Species that undergo reduction reaction are hydrogen, carbonic acid, water, and acid bicarbonate. Reduction reaction occurs by influenced electro-chemical reaction (activation reaction) and can also be determined by the reaction mass flow. For fluid flow there are two types of mass flow, the mass flow due to the reaction (corrosion product) and the outcome flow itself influenced by the characteristics of the fluid: Reynolds number, dynamic kinematics, density (Anderko & Young, 1999).

#### 2.2.2.1 Hydrogen ion reduction

To determine the effect of activation of the reaction and the mass flow of hydrogen reduction used the following equation (G.Keith, 2004) :

$$\frac{1}{i_H} = \frac{1}{i_{H,a}} + \frac{1}{i_{H,\lim}} \quad (2.10)$$

With it ( $H^+$ ) is the activation reaction ( $A/m^2$ ),  $i_{d \lim} (H^+)$  is the limiting diffusion current ( $A/m^2$ ) (limiting current). Reaction activation is formulated as:

$$i_H^o = i_H^* a_H^{0.5} a_{H_2O}^{2.2} \quad (2.11)$$

With  $c_t = 0529$  calculated from the equation by equation Nerst reduction of hydrogen ions and hydrogen atom reactions.

Activation reactions are affected by temperature is defined as:

$$i_H^* = i^* (T_{\text{reff}}) \exp \left[ -\frac{\Delta H}{R} \left( \frac{1}{T} - \frac{1}{T_{\text{reff}}} \right) \right] \quad (2.12)$$

Limiting current (limiting current) caused by the reaction of proton diffusion into the metal surface is calculated using the equation:

$$i_{H,\lim} = K_m F a_H \quad (2.13)$$

With  $K_m$  is the mass flow coefficient. Value  $K_m$  is calculated based on the diffusion coefficient of  $H^+$  and the viscosity of the solution.

### 2.2.2.2 Hydrogen ions produced by the reduction reaction of water

In addition, the reactions of Hydrogen ( $H^+$ ) are also affected by the water. Unlike what happened in the reduction of protons. Reduction of water does not flow so there is no flow limiting diffusion of water molecules ( $H_2O$ ) metal surface. And can be formulated as (G.Keith, 2004):

$$i_{H_2O}^o = i_{H_2O}^* a_H^{-0.5} a_{H_2O}^{2.2} \quad (2.14)$$

With the current exchange (exchange current density) is given by:

$$i_{H_2O}^* = i^*(T_{reff}) \exp \left[ -\frac{\Delta H}{R} \left( \frac{1}{T} - \frac{1}{T_{reff}} \right) \right] \quad (2.15)$$

### 2.2.2.3 Reduction of carbonic acid

Carbonic acid is a weak acid, so it can be assumed that in the reaction will produce hydrogen ions, thereby contributing effect limiting current (limiting current) hydrogen. Thus the equation for the hydrogen flow boundary becomes (G.Keith, 2004):

$$\frac{1}{i_{H_2CO_3}} = \frac{1}{i_{H_2CO_3,a}} + \frac{1}{i_{H_2CO_3,lim}} \quad (2.16)$$

Carbonic acid activation reaction is:

$$i_{H_2CO_3,a} = i_{H_2CO_3}^o \exp \left[ \frac{-\alpha_{H_2CO_3} F (E - E_H^o)}{RT} \right] \quad (2.17)$$

With the corrosion current H<sub>2</sub>CO<sub>3</sub> reduction is:

$$i_{H_2CO_3}^o = i_{H_2CO_3}^* a_{H_2CO_3} a_H^{-0.5} \quad (2.18)$$

Flow divider carbonic acid is also controlled by the reaction of hydration of CO<sub>2</sub> corrosion, as defined by Nescic and Vetter, yielding the following equation:

$$i_{H_2CO_3 \text{ lim}} = F[CO_2]_b (D_{H_2CO_3} k_{CO_2}^d k_{Hyd}^f)^{0.5} \quad (2.19)$$

### 2.3 THE EFFECT OF pH

pH is an indication of the  $H^+$  ion concentration in the solutions, which is one of the main species involved in cathodic reaction of  $CO_2$  corrosion process. It has been illustrated both experimentally and computationally that corrosion rate changes significantly with respect to pH. At low pH ( $pH < 4$ ) and low  $CO_2$  partial pressure ( $\leq 1$  bar), a flow sensitive direct reduction of  $H^+$  dominates the cathodic reaction. On the other hand, at higher pH ( $pH > 5$ ) and higher  $CO_2$  partial pressure ( $\geq 1$  bar) the cathodic reaction is controlled by the direct reduction of  $H_2CO_3$  which is related to the amount of dissolved  $CO_2$  (Lee, 2004). Therefore, higher pH will decrease the corrosion rate.

However, it is the indirect effect of pH on the formation of protective films (such as iron carbonate) that is the most important. Thus, increased precipitation rate, faster formation of protective films and reduction of the corrosion rate will be obtained (Lee, 2004).

### 2.4 THE EFFECT OF TEMPERATURE

Temperature quickens all the processes involved in  $CO_2$  corrosion including transport of species, chemical reactions in the bulk of the solutions and electrochemical reactions at the metal surface. Temperature can either increase or decrease the corrosion rate. In the case of corrosion where protective films do not form at low pH, corrosion rate increases with increasing temperature (Srdjan Nesic, 2002). The corrosion rate usually peaks somewhere in between  $60^\circ C$  and  $80^\circ C$  depending on flow conditions and water chemistry (Lee, 2004).

## 2.5 CORROSION PRODUCT FILM FORMATION

CO<sub>2</sub> corrosion of a metal is strongly dependent on the type of corrosion product film formed on the surface of the metal during the corrosion process. The stability, protectiveness, precipitation rate and the adherence of these films determine the rate of corrosion. Corrosion films can be form into three main elements that are Iron carbide (Fe<sub>3</sub>C), Iron carbonate (FeCO<sub>3</sub>) and Iron sulfide (FeS).

### 2.5.1 Iron carbide (Fe<sub>3</sub>C)

Iron carbide do not dissolved component of the mild steel that are left behind from the corrosion process. Iron carbide is conductive, very porous and non-protective. In corrosion process, iron carbide films can significantly affect by either decreasing the corrosion rate by acting as a diffusion barrier or increasing the corrosion due to galvanic coupling of the film to the metal, increase in the true specimen surface area and acidification of the solution inside the corrosion product film (Lee, 2004).

### 2.5.2 Iron carbonate (FeCO<sub>3</sub>)

The formation reaction of solid iron carbonate is given by (Lee, 2004) :



Solid iron carbonate precipitation occurs when the product of concentrations of Fe<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> exceed a certain limit known as the solubility limit. The rate of precipitation of iron carbonate is so slow. Then, most often the precipitation kinetics comes into consideration rather than the thermodynamics.

The equation for the rate of precipitation of the iron carbonate ( $R_{FeCO_3(S)}$ ) is given as:

$$R_{FeCO_3(S)} = \frac{A}{V} f(T) \cdot Ksp_{FeCO_3} \cdot f(S_{FeCO_3}) \quad (2.21)$$

Where Supersaturation  $S$  is defined as:

$$S_{FeCO_3} = \frac{c_{Fe^{2+}} \cdot c_{CO_3^{2-}}}{Ksp_{FeCO_3}} \quad (2.22)$$

With  $A/V$  = the surface area-to-volume ratio and  $Ksp_{FeCO_3}$  = solubility limit of  $FeCO_3$

Since  $CO_3^{2-}$  ion concentration is dependent on the pH, it can be assumed that:

$$S = f(Fe^{2+}, pH) \quad (2.23)$$

Iron carbonate precipitates drops the corrosion rate by presenting a diffusion wall for the species involved in the corrosion process and also blocking a portion of the steel and preventing electrochemical reactions from occurring at the steel surface.

The most significant reasons disturbing the precipitation of iron carbonate are supersaturation and the temperature.

### 2.5.3 Iron sulfide (FeS)

In the presence of  $H_2S$  the formation of iron sulfide can occurs. Formation reaction of solid iron carbonate is given by (Lee, 2004):



The precipitation of solid iron sulfide is assumed occurs when the product of concentrations of  $Fe^{2+}$  and  $S^{2-}$  exceed the solubility limit of  $FeS$ . The equation for the precipitation rate of the iron carbonate ( $R_{FeS(S)}$ ) is given as:

$$R_{FeCO_3(S)} = \frac{A}{V} f(T) \cdot K_{sp_{FeS}} \cdot f(S) \quad (2.25)$$

Where Supersaturation  $S_{FeS}$  is defined as:

$$S_{FeS} = \frac{c_{Fe^{2+}} + c_{S^{2-}}}{K_{sp_{FeS}}} \quad (2.26)$$

With  $K_{sp_{FeS}}$  = solubility limit of FeS

Iron sulfide affects the CO<sub>2</sub> corrosion is assumed in the same way as iron carbonate (by being a diffusion barrier and surface blockage). In some cases it has been observed that the presence of iron sulfide may lead to localized corrosion and the cause is still not clear because iron sulfide films are semi-conductive; (Lee, 2004).

## 2.6 THE EFFECT OF H<sub>2</sub>S

The CO<sub>2</sub> corrosion of mild steels in the presence of hydrogen sulfide (H<sub>2</sub>S) represents a major difficult for oil and gas production. The problem has become more important in the recent years as the available reserves of oil possess a considerable amount of H<sub>2</sub>S. Although the interactions of H<sub>2</sub>S with low carbon steels have been distributed by various authors, the effect of H<sub>2</sub>S understanding on CO<sub>2</sub> corrosion is still limited because the nature of the contact with carbon steel is complex (Lee, 2004).

In the presence of H<sub>2</sub>S, additional chemical reactions occurring in the bulk of the solution include:

Dissociation of dissolved H<sub>2</sub>S:

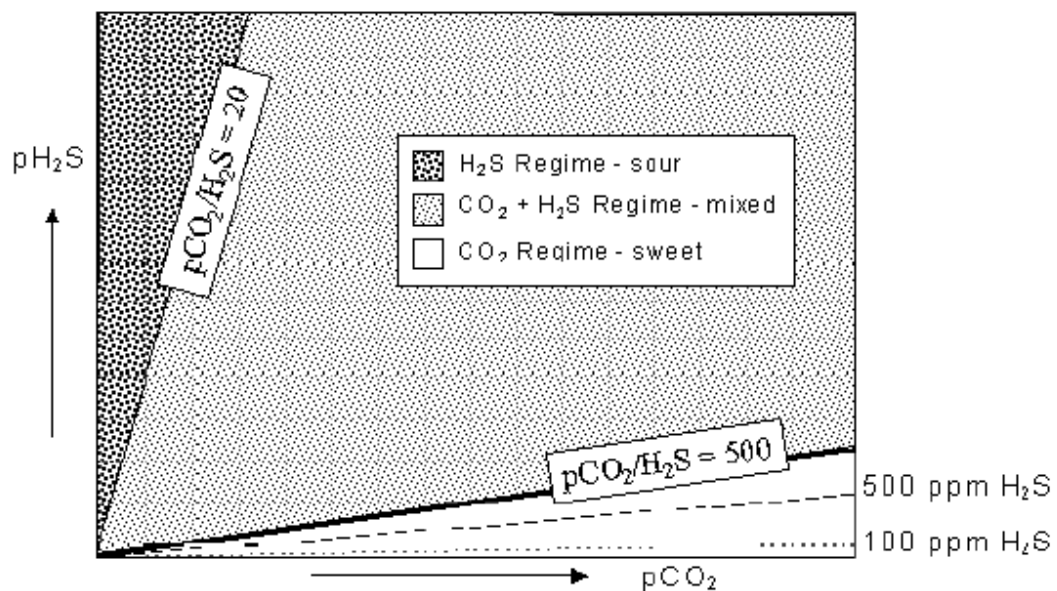


Dissociation of HS<sup>-</sup> ion:



$H_2S$  gas is near three times more soluble than  $CO_2$  gas, the acid formed by the dissociation of  $H_2S$  is about three times weaker than carbonic acid. Hence, the effect of  $H_2S$  gas is approximately the same as  $CO_2$  gas on decreasing the solution pH. Dissolved  $H_2S$  does not need to undergo the slow hydration step unlike dissolved  $CO_2$ , in order to become an acid.

Generally, three regimes in  $CO_2/H_2S$  system can be categorized based on the concentration of  $H_2S$  as shown in figure below:



**Figure 2.1:** Corrosion regimes in  $CO_2/H_2S$  corrosion defined by Pots, et al.

Source: Kun-Lin John Lee 2004