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Mechanistic model of stress corrosion cracking (scc) of carbon steel in acidic solution with the presence of H$_2$s

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Abstract. In oil and gas industrial environments, H$_2$S gas is one of the corrosive species which should be a main concern in designing infrastructure made of carbon steel. Combination between the corrosive environment and stress condition will cause degradation of carbon steel increase unpredictably due to their simultaneous effects. This paper will design a model that involves electrochemical and mechanical theories to study crack growth rate under presence of H$_2$S gas. Combination crack and corrosion propagation of carbon steel, with different hydrogen concentration has been investigated. The results indicated that high concentration of hydrogen ions showed a higher crack propagation rate. The comparison between corrosion prediction models and corrosion model developed by researchers used to verify the model accuracy showed a good agreement.

1. Introduction

Problems on corrosion in the oil and gas industry are, frequently, caused by H$_2$S gas. Those gases widely exist in the oil fields which can increase corrosiveness of the environments. Its existence is indicated as a source of early failures of the pipeline. Degree of corrosiveness of H$_2$S gases are influenced by environmental conditions such as temperature, CO$_2$ partial pressure, corrosion film properties and mechanical properties of the materials [1.2].
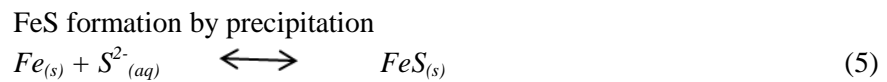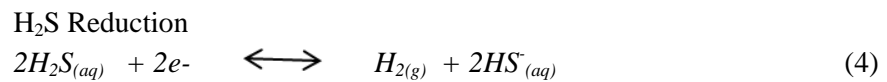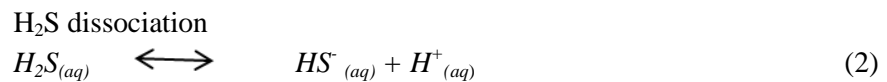
For structures applications, materials subjected to static and exposure to the corrosive environment, there will be continuous degradation of the structural material due to mechanical and electrochemical effects. Interaction between those corrosion and mechanical process involve electrochemical and deformation of the crack tip region as the crack is developing. Crack growth characteristics of materials can be used to determine the retaining strength and durability of the materials [3].

Many studies have been conducted to deal with these gases and can be found in open literature [1,4]. Because it is very important, many experiments and field studies of H$_2$S corrosion has been done to provide a better understanding of the aspects that affect the whole process. To date, the use of research using pure empirical method to find corrosion model equations are still preferable. However, the problem is further complicated as the corrosion can be influenced not only by setting parameters during experimental works. It is influenced by crack geometry, film properties, tip region, atomic dissolution, and direction of slip dislocation. The complex interactions of various species and operating conditions are difficult to simulate in the laboratory. Thus, the technical accuracy of corrosion prediction will deviate with the real mechanism. An approach of corrosion prediction using combination of mechanistic and empirical model can simulate the real data conditions.

2. H₂S corrosion

Hydrogen sulfide, when dissolved in water, is involved in a series of chemical reactions in the pipeline [5]:

H₂S dissolution

$$H_2S_{(g)} \longleftrightarrow H_2S_{(aq)} \tag{1}$$

H₂S dissociation

$$H_2S_{(aq)} \longleftrightarrow HS^-_{(aq)} + H^+_{(aq)} \tag{2}$$

HS- dissociation

$$HS^-_{(aq)} \longleftrightarrow H^+_{(aq)} + S^{2-}_{(aq)} \tag{3}$$

H₂S Reduction

$$2H_2S_{(aq)} + 2e- \longleftrightarrow H_{2(g)} + 2HS^-_{(aq)} \tag{4}$$

FeS formation by precipitation

$$Fe_{(s)} + S^{2-}_{(aq)} \longleftrightarrow FeS_{(s)} \tag{5}$$

The role of H₂S in changing behavior of corrosion rate was studied by [6,7]. The following are three numerical models constructed by some researchers.

3. Mathematical Model

A mechanistic model of uniform hydrogen corrosion can be modeled using fundamental physicochemical laws [1,8]. It consists of convective diffusion equation (6), molecular diffusion equation (7) and diffusion via solid film equation (8).

(i) Convective diffusion reactions (*flux*) through boundary layer are caused by mass transfer processes (K_m), bulk concentration (C_{bi}) and outer concentration (C_{oi}).

$$Flux_i = k_{m,i}\left(c_{bi} - c_{o,i}\right) \tag{6}$$

(ii) Molecular diffusion (*flux*) through the liquid in the porous outer scale:

$$Flux_i = \frac{D_i \varepsilon \Psi}{\delta_{oc}}\left(c_{oi} - c_i\right) \tag{7}$$

where, D_i is diffusion coefficient for dissolved species i (m²/s), ε is outer scale porosity, ψ is tortuosity factor, c_i is interfacial concentration of species *I*.

(iii) The very thin film and dense film at the metal surface forms a surface barrier. Then, solid state diffusion through the inner film can be formulated as:

$$Flux_i = A_i e^{\frac{B}{RT_K}} \ln\left(\frac{c_{i,i}}{c_{s,i}}\right) \tag{8}$$

Where, δf is film thickness, A is Arrhenius constant ,T_k is temperature (Kelvin),c_s is surface concentration, R is universal gas constant.

From the equations above, equation (1-8), expressed a mathematical corrosion theory *(CR)* as:

$$CR_i = A_i e^{\frac{B}{RT_K}} \ln \frac{c_{b,i} - CR_i \left(\dfrac{\delta_{oc}}{D_i \varepsilon \Psi} + \dfrac{1}{k_{m,i}} \right)}{c_{s,i}} \tag{9}$$

4. Electrochemical Theories

4.1. Anodic reaction
Based on the assumptions that dissolving metal ions into solution as a reaction is controlled by activation reaction, the equation reaction can be described as follows [8]:

$$i_{(Fe)} = i_{o,(Fe)} x 10^{\frac{\eta}{b_a}} \tag{10}$$

Where, b is tafel slope constant, i_o is current density, and η is polarisation potential.

4.2. Cathodic reaction
Cathode reactions occurring in the gas with some species undergo reduction reaction. Species that undergo reduction reactions are hydrogen, water, and acid bicarbonate (in the presence of CO_2 gas) as mentioned below.

4.3. Hydrogen ion reduction
To determine the effect of activation of the reaction and the mass flow of hydrogen reduction used the following equation (1) and equation (9):

$$\frac{1}{i_H} = \frac{1}{i_{H,a}} + \frac{1}{i_{H,\lim}} \tag{11}$$

Which $i_a(H^+)$ is reaction activations (A/m^2), $i_{lim}(H^+)$ is limiting current density (A/m^2).

4.4. Water reduction
The reaction of hydrogen ions (H$^+$) are also affected by the water. Reduction of water is formulated as follows:

$$i^o_{H2O} = i^*_{H2O} a_H^{-0.5} a_{H2O}^{2.2} \tag{12}$$

5. Mechanochemical Theories
The mechanochemical theories stated that a slip deformation is caused anodic dissolution at the bare surface which relates dislocation of slip plane, plastic shear and a constant stress [10] as expressed in the following equations.

$$\dot{\gamma} = \rho_d b \dot{X} \tag{13}$$

where ρ_d is the dislocation density, b is the Burgers vector and $\dot{X}$ is the average velocity of the dislocations. Then, crack tip strain rate at the tip, $\dot{\varepsilon}_{ct}$, is formulated as:

$$\dot{\varepsilon}_{ct} = 2\,\dot{\gamma}\,\cos\theta \tag{14}$$

where γ is plastic shear deformation, θ is the angle between the direction of the slip plane and tensile stress.

5.1. Anodic dissolution current density

The average current density of anodic dissolution at the crack tip, i_a, can be related to the crack tip potential corrosion. It promotes slip dissolution and repassivation at the material surface. A slip step, t_{slip}, consist of passive film and anodic ions dissolutions due to slip formation [10].

$$i_a = \frac{1}{t_{slip}} \int_0^{tslip} i(t)dt \tag{15}$$

5.2. Crack growth rate

Mechanism of slip formation and dissolution at the crack tip can be related to crack growth rate, *da/dt*. Based on Faraday's law, average current density by anodic dissolution can be expressed as:

$$\frac{da}{dt} = \frac{M}{ZF\rho_m} ia \tag{16}$$

Where *M* is the atomic weight of the metal and ρ is the metal density. By substituting Eq. (13 - 16), the SCC crack growth rate is expressed by equation (17 - 19).

$$\frac{da}{dt} = A_o \left(\frac{\varepsilon_{ct}}{C_m} \right)^n \tag{17}$$

$$A_0 = \frac{M}{zF\rho_m} \frac{i_0 t_0^n}{(1-n)} \tag{18}$$

$$C_m = 2\rho_d \cos\theta\, N_{slip} n_d b^2 \tag{19}$$

Where A_0 is the rate coefficient, C_m is the material factor constant, and n is the numerical constant, water conductivity, and corrosion potential.

6. Implementation of the Model

6.1. Effects of H$_2$S concentration

Mathematical model calculates indications of increasing corrosion rate due to hydrogen ions concentration based on formula from equation (9). Figure 1 shows a tendency of relationship between corrosion rate and hydrogen ion concentration.
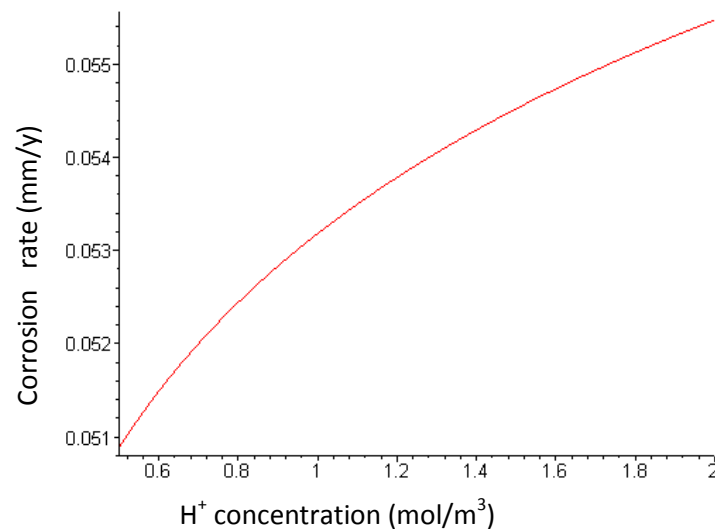
Figure 1. Simulated corrosion rate as a function of hydrogen ion concentration for a range of ions H^+ concentration from 0.4 mol/m^3 to 2 mol/m^3 at conditions: P_{total}= 1 bar and static.

It has been commonly accepted that the increase of time, corrosion current density will decrease exponentially. It becomes passive a certain period of time when film completely formed. But, at this condition, the films tend to dissolve which results corrosion rate start to grow. Figure 2 is a physical model used to describe corrosion and repassivation process. A mathematical relationship of current density and time used in this model is shown in figure 3.
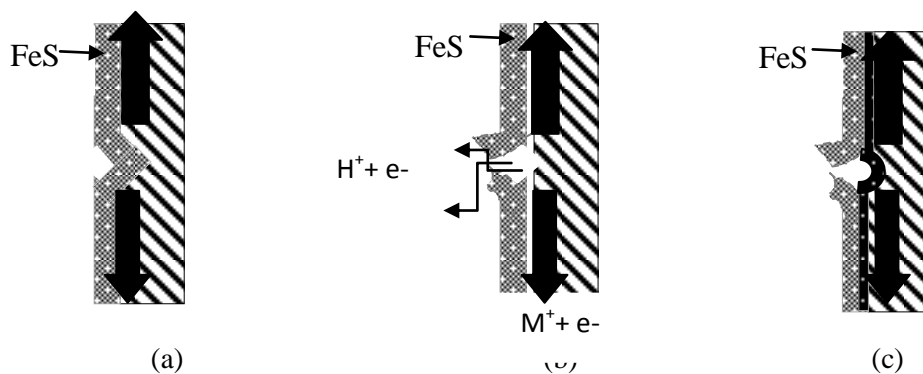

Figure 2. Models of film formation and film dissolution assumed at crack tip during corrosion process under stress condition. (a) Passive FeS film on crack tip (b) FeS film dissolution (c) FeS film formation.
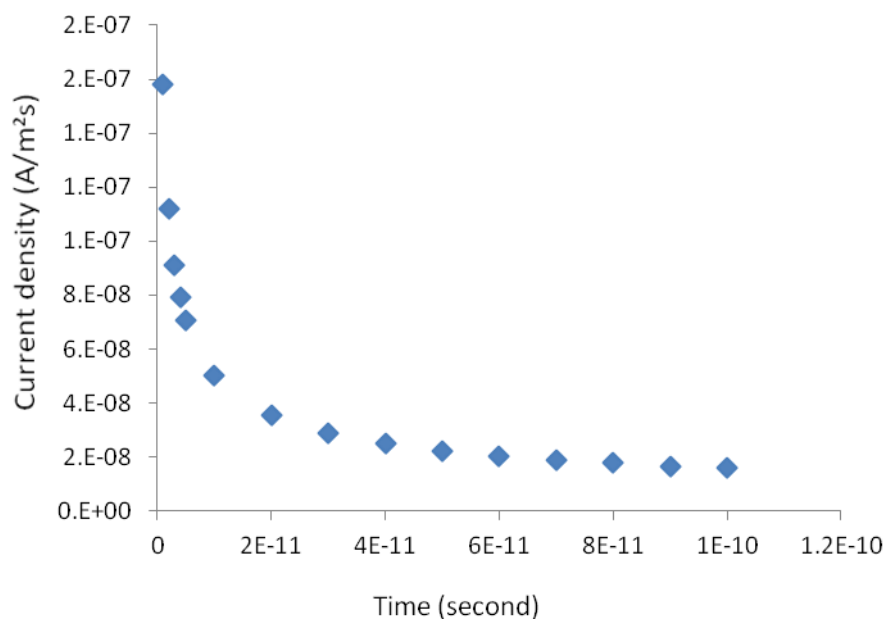
Figure 3. Current characteristic vs time of model at crack tip during corrosion.

Analytical observation from equation (17) indicates that crack growth has a decrease exponential function. This means that the corrosion rate decrease continuously within the SCC. The figures 4 shows a relationship between crack growth rate and material characteristics. Figure 5 present properties of dislocation densities related to crack growth rate.
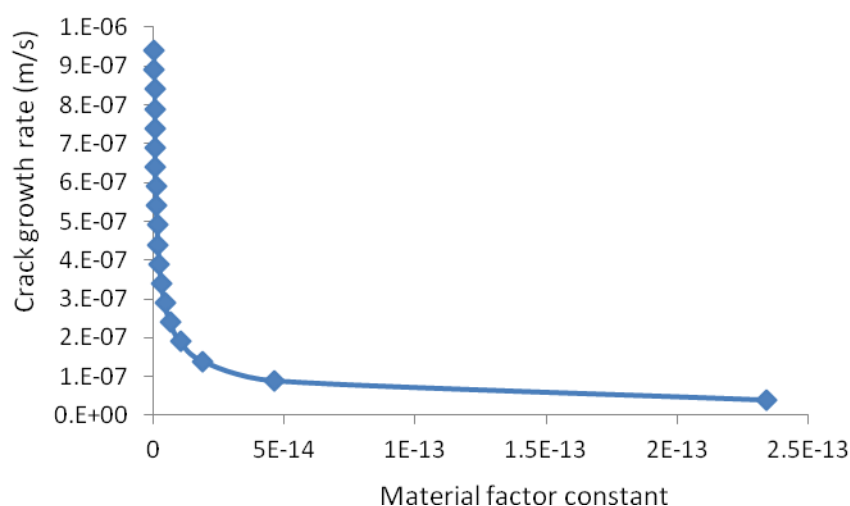

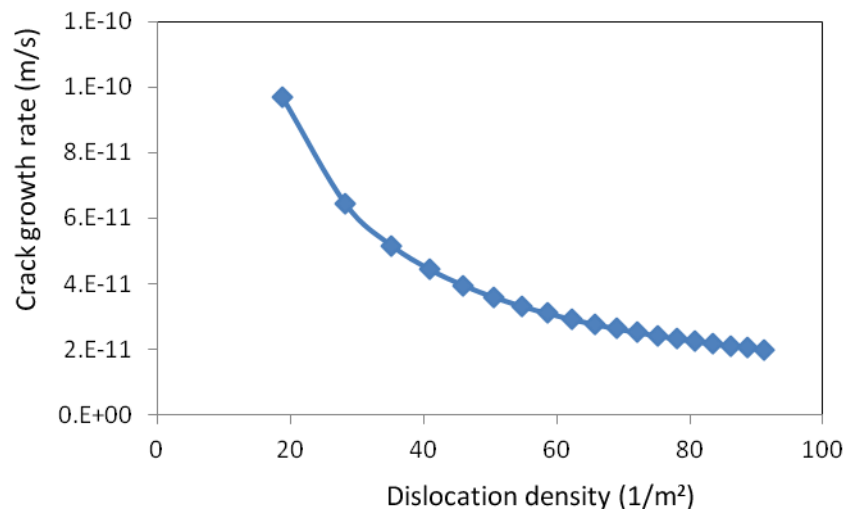**Figure 4.** Observed relationship between crack growth and material factor constant (*Cm*).

Figure 5. Observed relationship between crack growth and dislocation density.

7. Comparing models with published data experiments

Comparison experimental results are presented in this section to demonstrate the use of the model in determining crack extension during corrosion process. The data from calculations are validated using Irawan's experimental data [11] to assess the accuracy of the proposed model. The Irawan's experimental studies cover crack growth, corrosion current rate, and diffusion reaction rate. He used C ring samples materials with outer initial crack which were immersed in 1% - 3 % of H_2S solutions.
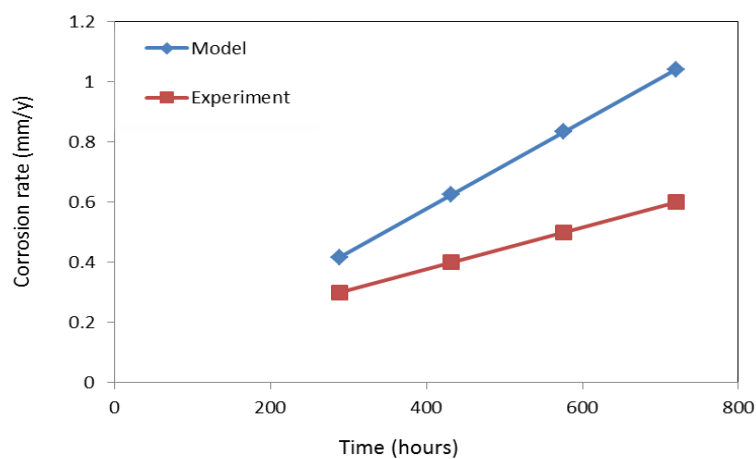

Figure 6. Comparison between the model to Irawan's experiment (in 1 % of H_2S saturated solutions at temperature 40^oC, pH 4, total pressure 1bar).

Figure 7. Comparison between the model to Irawan's experiment (in 2 % of H_2S saturated solutions at temperature 40^oC, pH 4, total pressure 1bar).

Figure 8. Comparison between the model to Irawan's experiment (in 3 % of H_2S saturated solutions at temperature 40^oC, pH 4, total pressure 1bar).
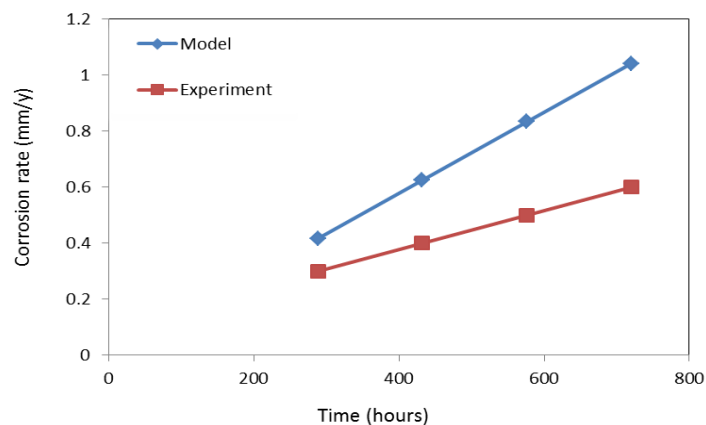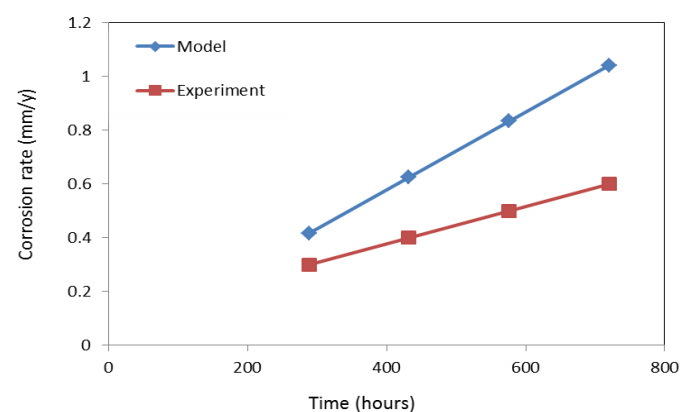
Figure 6, 7 and 8 show crack growth (caused by corrosion and stress) as a function of time at 1%, 2% and 3% of H_2S gas concentration. The figures compare corrosion rate calculated mathematically based on equations developed by researchers [1,7,8] and experimental data reported by [11]. The graphs (figure 6, 7 and 8) indicated that the corrosion rate will increase when H_2S concentration increased. The increasing corrosion rate was proportional to the time. From the figures, based on experimental data and model calculation, corrosion rate increased sharply at the higher H_2S gas concentration and lower H_2S concentrations. It seemed there were interactions between H_2S gas concentration and exposure time. Therefore, it can be concluded that H_2S was a more dominant factor in controlling corrosion behavior then factor of time. It means that effect of scaling formation, as a result of corrosion decrease, was not considered by majority corrosion prediction models. Figures show good agreement between experimental and calculated data based on this corrosion prediction model. Those three comparisons show good correlations, coefficient determinations and significant errors estimations which have similarity more than 95%.

8. Conclusion

In general, the use of numerical model has a benefit to simulate real conditions. Thus, complicated experiments can be reduced. Using mechanistic theories, relationship among the variables tested will be more simple in the form of mathematical equations. Thus, effects of independent variables will be easier to identify and to develop. Furthermore, using mathematical operations, the certain conditions such as stationary conditions can be calculated analytically. In H_2S corrosion, stationary point conditions can be used to indicate scaling formation, limiting current density and independent flow conditions.

It must be known that each model is suitable for certain condition and several assumptions have been made. This model involving the most variables input such as mass flow rate, scale effects, H_2S gas, as inputs parameters. Thus, this model gives a realistic approach to calculate corrosion rate in H_2S environments. Is is a simple model which measures corrosion rate in the worst cases. So, the corrosion rate result given is always higher. In associated with determination of scaling formation, Future work on optimization should be started with complex variables. The complex variables can be selected using design experiments to determine the important variables that can be developed further.

Acknowledgments

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