



# Simulation of CO<sub>2</sub> Corrosion of Carbon Steel in High Pressure and High Temperature Environment (HPHT)

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## Abstract

*In HPHT environments, the mechanism of CO<sub>2</sub> corrosion faces a challenge as an effect of chemical-physical reactions on the metal surface. The presence of other elements in the CO<sub>2</sub> system complicates corrosion behavior. To provide a realistic mechanism for corrosion process, some corrosion prediction models have developed software using fundamental theories such as electrochemical reactions and thermodynamics theories. Existing methods to predict corrosion rate models in HPHT environments have shown reasonable results. This paper reviews software of corrosion predictions which calculate corrosion rate based on mechanistic theories that study effects of H<sub>2</sub>S, acetic acid (HAc) concentrations, shear stress, pH in temperature from 25°C – 100°C and pressure from 1–10 bar. From the simulation, corrosion rate increased significantly in the high pressure CO<sub>2</sub> environment. Corrosion rate at pH 4 increased to 30 mm/y at a temperature from 15°C to 90°C. While at pH 8 corrosion rate reached 4 mm/y. This lower corrosion rate indicated a tendency for deposits formation at higher pH. Corrosion rate behaves in a different mechanism at high temperatures. The corrosion rate decreased to 4 mm/y when the temperature increased to more than 90°C. Effects H<sub>2</sub>S gas and HAc were identified to increase corrosion rate. Both elements provide extra cathodic reaction and create limiting current density in the cathodic reaction process based on polarization sweep models. However, the polarization graph calculated using corrosion models could not display passive behavior in the anodic polarization process. Thus, further, improvement should be considered. From the data calculation, it can be shown that corrosion prediction software can predict corrosion rate in HPHT conditions.*

## Keywords:

Carbon steel;  
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## INTRODUCTION

In oil and gas industries, CO<sub>2</sub> gas is considered the primary element that damages pipelines made of carbon steel. The gases can dissolve in the condensed water, which can reduce pH. Besides CO<sub>2</sub> gas, other elements such as H<sub>2</sub>S gas and Acetic Acid (HAc) are also found in oil and gas environments in many reservoir areas [1-10]. Research on CO<sub>2</sub> corrosion models has been developed by researchers [3, 4, 5]. They focused on the effects of environmental and material factors on corrosion rates [9][10]. Initially, the main type of corrosion studied was uniform corrosion. It was generally believed that the significant factors governing corrosion rate were the concentration of CO<sub>2</sub> and temperature. However, a further study has shown that corrosion products such as film formation can contribute to the corrosion process [10]. After

that period, models start to include the effects of scale formations in calculating corrosion rate [11].

Currently, models of corrosion rate have been more forward by considering complex factors involved in corrosion reactions, such as the effect of limiting current density, surface roughness, shear stress, thermos-chemical reaction, and water flow dynamics [14-23]. Combining existing elements cause corrosion process to occur in many ways and in several mechanisms. Understanding corrosion mechanism of those mixed elements requires reasonable corrosion models. Models for CO<sub>2</sub> corrosion have been developed through experiments and numerical theories [1-20].

In the form of semi-empirical correlations, researchers used electrochemical and thermodynamic theories, including iron dissolution, limiting current density, and activation reaction of dissolved ions. In HPHT environments, CO<sub>2</sub> corrosion faces a challenge as an effect of iron carbonate scales which can interfere corrosion rate. Furthermore, when H<sub>2</sub>S is present in the CO<sub>2</sub> system, corrosion model will vary based on H<sub>2</sub>S concentration [12, 14, 23, 27, 35].

Experimental studies performed by various authors [4, 21, 35] stated the effects of H<sub>2</sub>S on cathodic and anodic processes and the formation of various crystalline forms of iron sulfide scales. Thus, the effect of H<sub>2</sub>S gas on corrosion rate determined by its concentration. In addition, a weak acid, HAc, is also found to contribute corrosion rate. HAc concentration levels have been incorporated into the study as a key parameter [4, 8, 19, 20]. There are corrosion prediction models offered by industries that can be used to calculate carbon steel corrosion as discussed to accommodate these complex variables

## MATERIAL AND METHOD

There are corrosion prediction models offered by industries that can be used to calculate carbon steel corrosion. Some of them will be discussed here.

NORSOK [28] standard is owned by the Norwegian Oil Industry Association and Federation of Norwegian Manufacturing Industries. The program only covers corrosion rate calculations where CO<sub>2</sub> is the corrosive agent. It does not include the corrosivity, e.g., contamination of O<sub>2</sub>, H<sub>2</sub>S etc. The model is an empirical containing CO<sub>2</sub> at different temperatures, pH, CO<sub>2</sub> fugacities, wall shear stresses, and temperatures from 20 to 160°C.

$$CR_t = K_t x f CO_2^{0.62} x (S/19)^{0.146+0.0324 \log(f CO_2)} x f(pH) t \quad (1)$$

Where C.R. is the corrosion rate (mm/yr), K<sub>t</sub> is the constant for the temperature t, f CO<sub>2</sub> is the fugacity of the CO<sub>2</sub> (bar), S is Wall shear stress (Pa), f(pH)t is the pH factor at temperature.

Multicorp uses oil wetting and crude oil chemistry effects as parameters [25]. It contains an interface where the model developed by the institute for corrosion and multiphase technology, Ohio University's Research [25]. Wettability properties are based on the model published by Wang. [34]. Critical velocity for entraining free water by the flowing oil phase is used as the key variable. It also includes a phase inversion point and the flow pattern determination. Phase inversion calculations are based on the viscosities of the crude oil and water phases.

E.C.E. model considers the oil wetting correlation described in the equation based on field correlation. For low horizontal flow are used velocities < 1 m/s, the F<sub>oil</sub> = 1 [18]. The water cut is not important in influencing the actual corrosion rate at low velocities. E.C.E. program software calculates corrosion rate based on a method developed by de Waard and Williams. The modified formula recommended was referring to C. de Waard, U. Lotz and A. Dugstad paper presentation [17]. They proposed a corrosion prediction expression as:

$$V_{cor} = \frac{1}{\frac{1}{V_r} + \frac{1}{V_m}} \quad (2)$$

Where  $V_r$  is corrosion reaction and  $V_m$  is mass transfer effect. The reaction corrosion is:

$$\log(V_r) = 4.84 - \frac{1119}{t + 273} + 0.58 \log(f_{CO_2}) - 0.34 (pH_{act} - pH_{CO_2}) \quad (3)$$

And the mass transfer variable is defined as:

$$V_m = 2.8 \frac{U^{0.8}}{d^{0.2}} f_{CO_2} \quad (4)$$

Where  $T$  is the temperature ( $^{\circ}C$ ),  $p_{CO_2}$  is pressure (bar),  $f_{CO_2}$  is fugacity  $CO_2$  (bar),  $pH_{CO_2}$  is the pH of pure water saturated with  $CO_2$  at prevailing temperature and pressure. The fugacity of  $CO_2$  is similar to its partial pressure but corrected for non-ideality of  $CO_2$  at high pressure and temperature. The mass transfer represents the main part of the dependence on flow velocity  $U$  and pipe diameter  $d$ .

Cassandra is a model to implement de Waard and B.P.'s experiences [15]. The input includes pH,  $CO_2$  concentration, temperature, and water contaminant. This model does not consider a scaling temperature. The user must set an assumption of scaling temperature:

$$\log(V_r) = 5.8 - 1710/T + 0.67 \log(P_{CO_2}) \quad (5)$$

## RESULTS AND DISCUSSION

### Prediction of $CO_2$ Corrosion Rate

#### *Effect of pH on $CO_2$ corrosion rate in HPHT environment*

Effects of temperature and temperature on corrosion rate in  $CO_2$  gas environments are presented in Figure 1. As calculated by Cassandra, the effect of temperature varied from  $25^{\circ}C$  to  $90^{\circ}C$ . There was a clear acceleration of corrosion rates with increased temperature in both pH 4 and pH 8. The corrosion rate increased, at pH 4, to 20 mm/y in the range of temperature from 25 to  $90^{\circ}C$ . At the same time, it increased 3 mm/y at pH 8 at the same range of temperature. Comparing effects of pH, corrosion rate reduced significantly at pH 8 compared to corrosion rate at pH 4. The low corrosion rate at pH 8 showed the formation of scale. These observations agree with some studies carried out in the past founding [16, 23, 26, 34, 35]. An increase in pH will cause the film to become thicker, denser and passivate anodic reaction.

#### *Effect of shear stress on $CO_2$ corrosion rate in HPHT environment*

The corrosion rate of carbon steel at various shear stress, pressure and temperature are shown in Figure 2a and Figure 2b successively. At the temperature of  $100^{\circ}C$ , pH 4 and saturated  $CO_2$  gas at 10 bars, the corrosion rate increased when pressure and shear stress increased (Figure 2a). Similar trends were also seen at the pressure of 10 bar, pH 4 and saturated  $CO_2$  (Figure 2b). In addition, the corrosion rate increased when shear stress increased. Investigators [23, 25, 26, 30, 31] explained that the effects of shear stress caused by fluid velocity on corrosion rate are associated with higher turbulence and mixing in the solution. Therefore, it affects the corrosion rate of the carbon steel surface and the iron carbonate film. However, temperature affects corrosion rate differently. At temperatures below  $80^{\circ}C$ , hydrogen evolution acts as the rate determining step. At temperatures above  $80^{\circ}C$ , dense and protective films are produced to reduce corrosion rate.

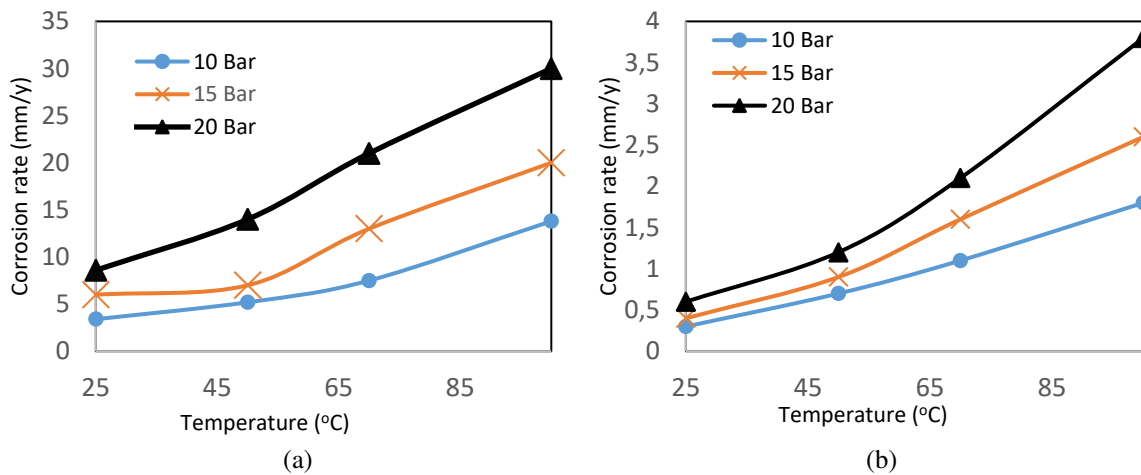


Figure 1. Corrosion rate at various temperatures and pressure at pH 4 (a), pH 8 (b) and saturated CO<sub>2</sub> gas as calculated by Cassandra [15]

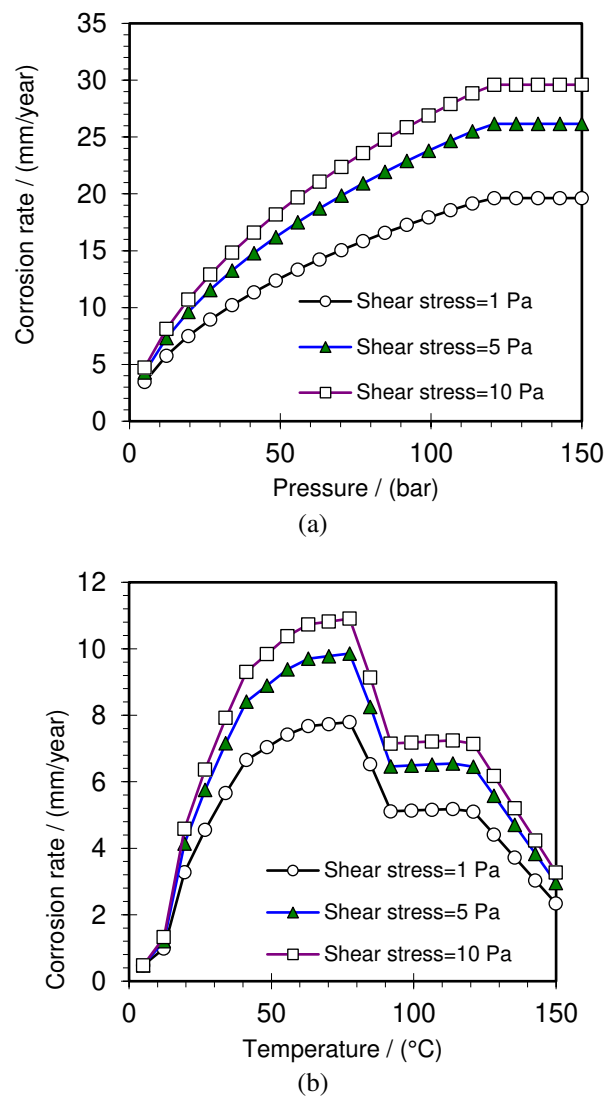


Figure 2. Effects of pressure (a) and temperature (b) on corrosion rate at varying shear stress as calculated by Norsok (CO<sub>2</sub> saturated solutions, 10 bar, pH4, and 100°C) [28]

The effect of pH on the corrosion rate was studied in solutions saturated with CO<sub>2</sub> in the pH range from 4 to 6 (Figure 2a and Figure 2b). As the pH increases from 4 to 6, the anodic reaction rate increases, consistent with Bockris's iron dissolution mechanism [13]. This is expected since, with the increase of the pH, the concentration of the hydrogen ion decreases. In addition, the pH of wet gas in the CO<sub>2</sub> system is often assumed equal to the saturation of FeCO<sub>3</sub> precipitation. Therefore, an increase in pH will cause the film to become thicker, denser and more protective.

#### Mechanistic Study of CO<sub>2</sub>/H<sub>2</sub>S Corrosion

The role of H<sub>2</sub>S elemental is believed to influence corrosion rate. Figure 3 shows that increasing H<sub>2</sub>S concentration causes higher cathodic polarization and corrosion potential. It was studied by Brown [14] that the effects of concentration of high H<sub>2</sub>S in CO<sub>2</sub> will increase corrosion rate compared to a solution with a small concentration of H<sub>2</sub>S. Kun-Lin was working with 10 ppm H<sub>2</sub>S found that scale formed on the surface has a role in inhibiting corrosion rate. From the Figure 3, it can be seen that the corrosion rate is under charge-transfer control as an effect of H<sub>2</sub>S concentration. The addition of H<sub>2</sub>S also impacts diffusion limiting the current density of CO<sub>2</sub> corrosion.

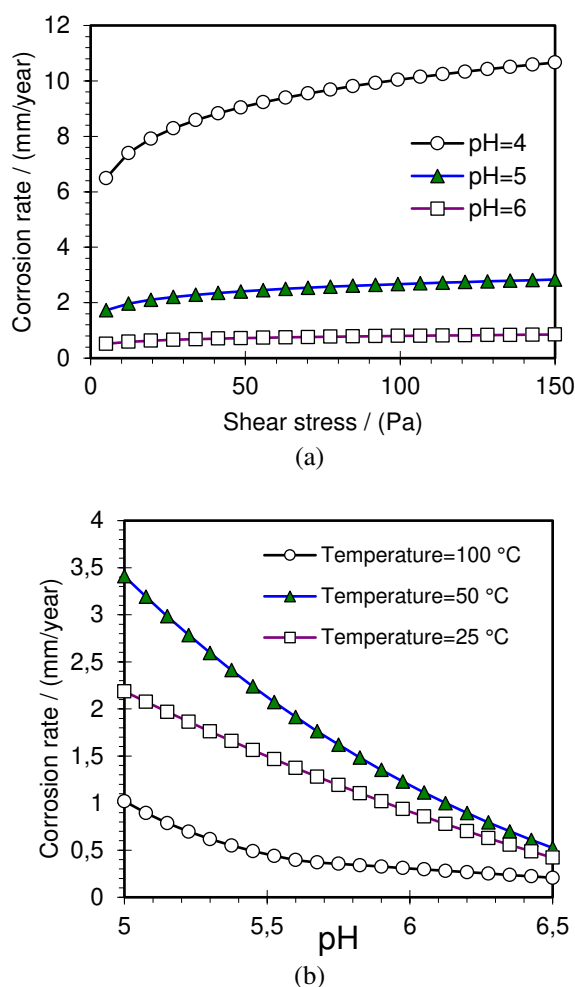


Figure 3. Effects of shear stress (a) and pH (b) on corrosion rate at CO<sub>2</sub> saturated solutions as calculated by Norsok [28] (10 bar, 100°C (a) and (6 bar, 1 pa shear stress (b)).

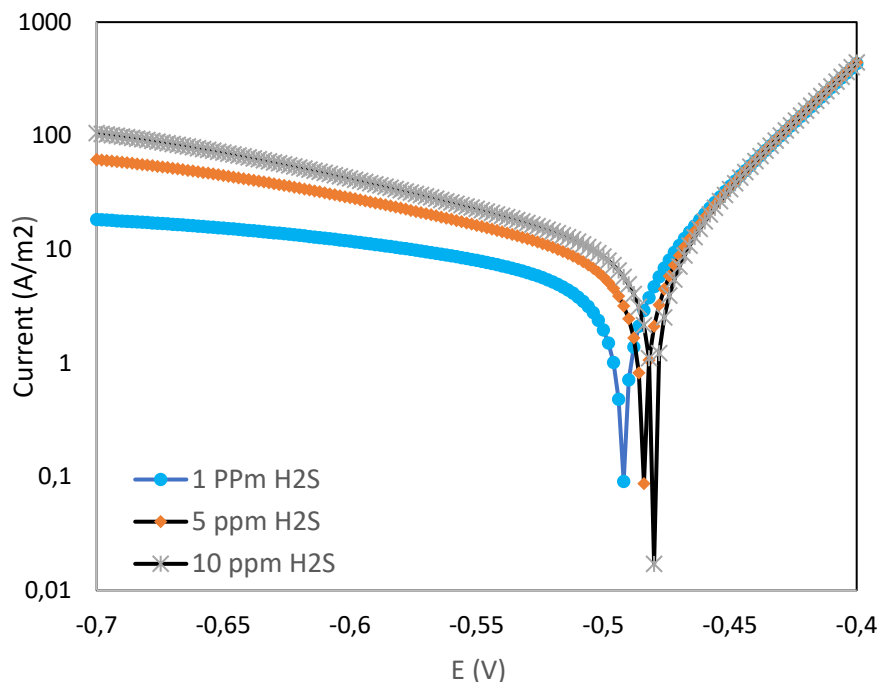


Figure 4. Potentiodynamic sweeps in 1 – 100 ppm H<sub>2</sub>S, CO<sub>2</sub> saturated solution. at temp. 90°C, pressure 10 bar, pH 4, stagnant as calculated by Freecorp [19]

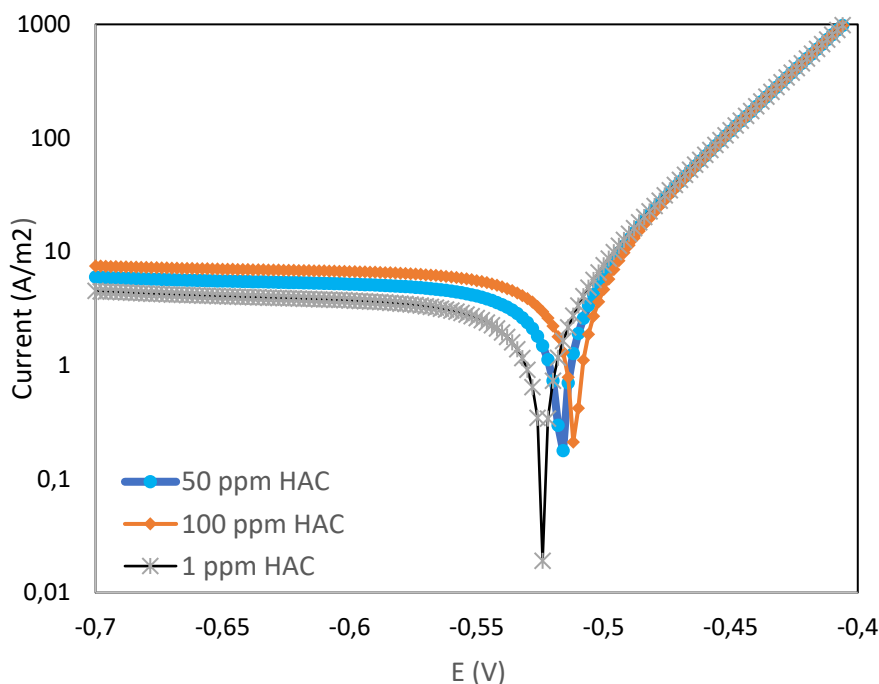


Figure 5. Potentiodynamic sweeps in 1 ppm HAC – 50 ppm HAC, CO<sub>2</sub> saturated solution. at temp. 90°C, pressure 10 bar, pH 4, stagnant as calculated by Freecorp [19]

#### *Mechanistic Study of CO<sub>2</sub>/HAc Corrosion*

The other species, such as Acetic Acid (HAc) will also contribute to the corrosion rate. Studies [1-10, 26, 33, 34, 35, 36] have demonstrated that those multi-species factors can govern the corrosion process and in several mechanisms. The effect of HAc on the corrosion rate of carbon steel has been studied by many researchers [1-10, 23]. Figure 4 and Figure 5 present



polarization sweep to research the effect of HAc on corrosion rate. Martin [23] pointed out that CO<sub>2</sub> induced acidification can also cause partial re-association of anions. Such weak acids, HAc can increase the oxidizing of H<sup>+</sup> by raising the limiting diffusion current for cathodic reduction. The presence of this acid also will tend to solubilise the dissolving iron ions [26]. The electrochemical behavior of carbon steel on the additions of HAc has shown that the presence of HAc in the solution decreases pH, increases the cathodic limiting current, and decreases E<sub>corr</sub> [23].

## CONCLUSION

In general, all models confirmed that CO<sub>2</sub> caused a higher corrosion rate. Thus, in HPHT CO<sub>2</sub> environments, carbon steel is not recommended. With a pressure of more than 10 bar and a temperature of higher than 100°C, the corrosion was higher than 10 mm/y. The CO<sub>2</sub> corrosion process was accelerated with the presence of H<sub>2</sub>S gas and HAc ions. H<sub>2</sub>S and HAc have shown interferences in corrosion mechanism by facilitating limiting current density on cathodic reaction. Both elements also resulted in an extra cathodic reaction. In addition, shear stress increased corrosion rate through flow motion which impinged metal surface. In contrast with the effect of pH, pH catalyzed solution for film formation to retarded corrosion process.

## ACKNOWLEDGMENTS

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