Development of a Prediction Model for High pCO$_2$ Corrosion of Mild Steel

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ABSTRACT

Most of the corrosion prediction models used for design of oil and gas lines carrying high pCO$_2$ are valid up to 1 ~ 2 MPa of pCO$_2$ and are very conservative at higher pCO$_2$ because they do not account for the effect of high pCO$_2$ on the water chemistry and the corrosion mechanism. The present work was focused on developing a predictive tool for near-critical and supercritical CO$_2$ corrosion of mild steel. It incorporates changes in the water chemistry module due to update solubility and dissociation equations, changes in the electrochemical module due to the presence of a thick and porous corrosion product layer, and consideration of an adsorption mechanism for H$_2$CO$_3$ at the steel surface. The comparison between experimental results and model predictions showed a good agreement under various pressure and temperature ranges.

Key words: Supercritical CO$_2$, CO$_2$ corrosion, carbon steel, corrosion model

INTRODUCTION

Internal corrosion of carbon steel pipeline in high partial pressure CO$_2$ (pCO$_2$) environments have gained more interest recently relating to carbon capture and storage (CCS), enhanced oil recovery (EOR), and deep water oil and gas production applications. Although there are extensive research data available on high pCO$_2$ corrosion, minimal information has been reported in the literature that could aid in
establishing a corrosion model for carbon steel in such conditions. Furthermore, the published literature on supercritical CO\textsubscript{2} primarily addresses topics related to sequestration and enhanced oil recovery (EOR) that usually involve “dry” gases where water is only present at the ppm level.

The impact of aqueous CO\textsubscript{2} corrosion on carbon steel has been studied extensively at pressures relevant for oil and gas transport (up to 2 MPa CO\textsubscript{2}). Therefore, most of the predictive models used for design of oil and gas lines carrying high pCO\textsubscript{2} are valid up to 1 ~ 2 MPa of pCO\textsubscript{2} and are very conservative at higher pCO\textsubscript{2}. It has been reported that aqueous corrosion mechanisms in high pCO\textsubscript{2} are similar to those in low pCO\textsubscript{2} conditions including characteristics of corrosion product layer and the response of corrosion rate with temperature. This indicates that the existing CO\textsubscript{2} corrosion model could be used to predict the corrosion rate at high pCO\textsubscript{2} conditions with some modifications in chemical, electrochemical or transport processes. For example, since CO\textsubscript{2} changes from gaseous to liquid or supercritical with increasing pressure, it will lead to different interaction with water, i.e. CO\textsubscript{2} solubility in water will not follow Henry’s law in liquid or supercritical CO\textsubscript{2} conditions, which results in changing water chemistry.

Thus, the objective of the present study was to develop a predictive model for high pCO\textsubscript{2} corrosion of mild steel considering with changes in chemical and electrochemical reactions.

**MODEL DESCRIPTION**

The mechanistic model developed by Nesic et al., in early 2000 covers most of the key processes present in uniform CO\textsubscript{2} corrosion of carbon steel: electrochemical reactions at the steel surface, chemical reactions and transport of species between the steel surface and the bulk solution, and formation/growth of iron carbonate (FeCO\textsubscript{3}) layer. The physical, mathematical, and numerical aspects of the model are explained in detail in the previous papers. In the present study, this model was used as a base platform and the key aspects of the model are briefly described below:

**Water Chemistry Model**

Understanding water chemistry is an important precondition for predicting CO\textsubscript{2} corrosion of carbon steel. Various chemical reactions take place in the water phase due to the presence of CO\textsubscript{2}. For a CO\textsubscript{2} aqueous system, the following reactions are taken into consideration at all times:

\[
\text{CO}_2(g) \Leftrightarrow \text{CO}_2(aq) \quad (\text{Dissolution of CO}_2) \quad (1)
\]

\[
\text{CO}_2(aq) + \text{H}_2\text{O} \Leftrightarrow \text{H}_2\text{CO}_3 \quad (\text{Hydration of aqueous CO}_2) \quad (2)
\]

\[
\text{H}_2\text{CO}_3 \Leftrightarrow \text{H}^+ + \text{HCO}_3^- \quad (\text{Dissociation of carbonic acid}) \quad (3)
\]

\[
\text{HCO}_3^- \Leftrightarrow \text{H}^+ + \text{CO}_3^{2-} \quad (\text{Dissociation of bicarbonate ion}) \quad (4)
\]

\[
\text{H}_2\text{O} \Leftrightarrow \text{H}^+ + \text{OH}^- \quad (\text{Dissociation of water}) \quad (5)
\]

The reactions shown above can be described by equilibria reactions as follows based on the assumption of infinite dilution:

\[
K_{\text{sol}} = \frac{c_{\text{CO}_2(aq)}}{P_{\text{CO}_2(g)}} \quad (6)
\]

\[
K_{\text{hyd}} = \frac{c_{\text{H}_2\text{CO}_3}}{c_{\text{CO}_2}c_{\text{H}_2\text{O}}} \quad (7)
\]

\[
K_{\text{ca}} = \frac{c_{\text{H}^+}c_{\text{HCO}_3^-}}{c_{\text{H}_2\text{CO}_3}} \quad (8)
\]
where $C_{CO_2}$, $C_{H_2CO_3}$, $C_{HCO_3}$, $C_{CO_3^{2-}}$, $C_{H^+}$, and $C_{OH^-}$ are the concentrations (mol/L) of CO$_2$, carbonic acid, bicarbonate ion, carbonate ion, hydrogen ion, and hydroxide ion, respectively.

The equilibrium constants, $K$, are a function of the temperature and are available in the open literature. Since the solution cannot have a net charge, an electroneutrality relation is required. Mathematically, it is expressed:

$$C_{H^+} = C_{HCO_3^-} + 2 \times C_{CO_3^{2-}} + C_{OH^-}$$

**Electrochemical Model**

As the CO$_2$ corrosion process is electrochemical in nature, the corrosion rate can be explicitly determined by calculating the rate of the electrochemical reactions occurring simultaneously at the steel surface:

**Anodic (oxidation) reaction:**

$$Fe \rightarrow Fe^{2+} + 2e^-$$

**Cathodic (reduction) reactions:**

$$H^+ + e^- \rightarrow \frac{1}{2}H_2$$
$$H_2CO_3 + e^- \rightarrow \frac{1}{2}H_2 + HCO_3^-$$

The electrochemical reaction rate can be expressed as a current density, $i$ (expressed in $A m^{-2}$), which is a function of the potential at the metal surface, $E$ (expressed in $V$):

$$i = \pm i_0 \times 10^{\frac{E-E_{rev}}{b}} \times \prod_{s=1}^{n_a} (1-\theta_s)$$

This equation is unique for each of the electrochemical reactions involved in a corrosion process such as iron oxidation, hydrogen reduction and carbonic acid reduction. The “+” sign applies for anodic reactions while the “-” sign applies for cathodic reactions. $\theta_s$ is the fraction of the steel surface where a given electrochemical reaction does not occur because the surface is covered by a species $s$ which could be an adsorbed inhibitor or a protective film. The product sign $\prod$ accounts for a compounding (additive) effect by more than one surface species. For each electrochemical reaction, Equation (1) is different because of the parameters defining it: $i_0$ - the exchange current density in $A m^{-2}$, $E_{rev}$ - the reversible potential in $V$, and $b$ – the Tafel slope in $V$. These parameters have to be determined experimentally and are functions of temperature and in some cases species concentrations. The unknown potential at the metal surface $E$ in Equation (15), is also called the corrosion potential or open circuit potential, which can be found from the charge balance equation at the metal surface:

$$\sum_{a=1}^{n_a} i_a = \sum_{c=1}^{n_c} i_c$$

where $n_a$ and $n_c$ are the total number of anodic and cathodic reactions respectively.

**FeCO$_3$ Layer Formation and Growth Model**

Solid FeCO$_3$ forms when the concentrations of Fe$^{2+}$ and CO$_3^{2-}$ exceed the solubility limit according to the following reaction:

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Fe^{2+}\text{(aq)} + CO_3^{2-}\text{(aq)} \leftrightarrow \text{FeCO}_3\text{(s)} \tag{17}

When FeCO_3 precipitates on the steel surface, it can slow down the corrosion process not only by presenting a diffusion barrier for the species involved in the corrosion process but also by blocking a portion of the steel surface and preventing the underlying steel from further corrosion.

The governing equation for FeCO_3 layer growth based on mass conservation of FeCO_3 in the solution is shown in equation (18).

\[
\frac{\partial \varepsilon}{\partial t} = \frac{M_{\text{FeCO}_3} A}{\rho_{\text{FeCO}_3} V} R_{\text{FeCO}_3} - CR \frac{\partial \varepsilon}{\partial x} \tag{18}
\]

where \( \varepsilon \) is porosity, \( t \) is time, \( M_{\text{FeCO}_3} \) is molar mass of FeCO_3, \( \rho_{\text{FeCO}_3} \) is density of FeCO_3, \( \frac{A}{V} \) is area-volume ratio, \( R_{\text{FeCO}_3} \) is precipitation rate of FeCO_3, \( CR \) is corrosion rate, and \( x \) is distance. In this equation, FeCO_3 layer growth is characterized by the change in porosity (\( \varepsilon \)), which changes between 0 and 1. A value of 1 indicates that no FeCO_3 layer forms while a value of 0 represents that the surface is completely filled with FeCO_3. This equation suggests that the growth of FeCO_3 layer is attributed to two factors: FeCO_3 precipitation and undermining steel corrosion. Depending on the relative values of these two terms, FeCO_3 layer can be either protective or non-protective.

RESULTS AND DISCUSSION

Modification in Water Chemistry Model

In low pCO_2 system, the concentration of dissolved CO_2 in water is directly proportional to its partial pressure (Equation 1). The solubility constant is calculated and derived using Henry’s constant (\( K_{\text{sol}} \)) as the concentration of dissolved CO_2 is relatively small. In high pCO_2 systems, however, the relationship between concentration and pressure is not linear and Henry’s law cannot be used directly. Instead, the non-ideality of the CO_2 phase must be taken into account. In the present study, two different CO_2 solubility models were selected from open literature for high pCO_2 conditions and compared with the case with Henry’s law. Figure 1 shows the comparison of mole fraction of CO_2 in water as a function of pCO_2 calculated from different solubility models at 25°C and 60°C. It shows that the amount of dissolved CO_2 increased with increasing pCO_2. It can be also seen that as pCO_2 increases, the solubility of CO_2 in water deviates further from Henry’s Law; that is, the domain of validity of Henry’s Law is at best 2 MPa at 25°C, and only 0.8 MPa at 60°C. In addition, there is no significant difference in CO_2 content between the high pCO_2 solubility models.
Figure 1: Comparison of the calculated molar fraction of dissolved CO$_2$ in water based on Henry’s law and high pCO$_2$ solubility models as a function of pCO$_2$: (a) 25°C, (b) 60°C.

Other equilibrium constants were also compared between low pCO$_2$ and high pCO$_2$ models. For example, the equilibrium constant for carbonic acid dissociation ($K_{ca}$) is calculated in the low pCO$_2$ model as:

$$K_{ca} = 387.6 \times 10^{-(6.41-1.594\times10^{-3}T_f+8.52\times10^{-6}T_f^2-3.07\times10^{-5}p-0.4772\times T_f+0.118\times I)}$$

where $T_f$ is the temperature in degrees Fahrenheit, $p$ is the pressure in psi and $I$ is the ionic strength in molar. For the high pCO$_2$ model, $K_{ca}$ was taken from open literature that can cover the temperature range of 0°C to 100°C and the pressure range of 0.1 to 300 MPa:

$$\ln K_{ca} = 233.5159304 - 11974.383487^{-1} - 36.50633536 \ln T + (-45.08004597T^{-1} + 2131.18848T^{-2} + 6.7142562997T^{-1} \ln T)(P - P_s) + (0.0083939152127^{-1} - 0.4015441404\times T^{-2} - 0.00124018735T^{-1})(P - P_s)^2$$
where $P_s$ is the saturation pressure of water, $P$ is the CO$_2$ pressure in bar, and $T$ is the temperature in Kelvin. Figure 2 compares the $pK_{ca}$ values as a function of pCO$_2$ calculated by Equation 16 and Equation 17 at 25°C and 60°C. Although the $pK_{ca}$ of high pCO$_2$ model was slightly higher than that of low pCO$_2$ model, it will not cause a significant difference in the calculation of species concentrations. The same trend was observed for the comparison of other equilibrium constants between low pCO$_2$ model and high pCO$_2$ model.

![Figure 2](image)

**Figure 2**: Comparison of the $pK_{ca}$ calculated by low pCO$_2$ model and high pCO$_2$ model as a function of pCO$_2$ at 25°C and 60°C.

Figure 3 shows the pH values as a function of pCO$_2$ calculated by low pCO$_2$ model and high pCO$_2$ model at 25°C and 60°C. The pH values decreased with increasing pCO$_2$ due to the increase of the dissolved CO$_2$ amount (Figure 1). However, a significant effect of non-ideal behavior of CO$_2$ at high pressures on the pH can be seen due to the deviation from the solubility calculations based on Henry’s law and the high pCO$_2$ solubility model. This result suggests that utilizing the low pCO$_2$ water chemistry model could overestimate the corrosion rate in high pCO$_2$ conditions due to the inaccurate prediction of pH.

![Figure 3](image)
Modification in Electrochemical Model

The modified water chemistry model was implemented and the corrosion rate was predicted in conjunction with the original electrochemical model. However, the corrosion rates were still over-predicted as compared to experimental data by a factor of 2 to 4.

If the species concentrations are predicted correctly with the high pCO$_2$ water chemistry model, then the over prediction of corrosion rates may be a result of not considering the limited ability for the corrosive species to adsorb on the steel surface in order to be reduced. In other words, it can be assumed that all the increased concentrations of species, such as H$^+$ and H$_2$CO$_3$ due to the increase in pCO$_2$ can not adsorb to the metal surface due to the reaction site limitations. Therefore, the cathodic reduction reactions become limited by adsorption kinetics resulting in plateau for the corrosion rate at high pCO$_2$ conditions. This phenomenon was implemented using a Langmuir adsorption isotherm:

$$\theta = 1 - \frac{K_p pCO_2}{1 + K_p pCO_2}$$

where $\theta$ is the fractional surface coverage for species at the steel surface, and $K$ is the adsorption equilibrium constant. The value of $\theta$ determines availability of the reducible species at the surface. Figure 4 shows the fractional surface coverage coefficient as a function of pCO$_2$.

Since H$_2$CO$_3$ is by far the main cathodic species in the corrosion reaction at high pCO$_2$ conditions (as compared to H$^+$), the implementation of the adsorption coefficient $\Theta$ has been applied to the calculation of the current density of H$_2$CO$_3$ reduction reaction. This will reduce the influence of H$_2$CO$_3$ on the corrosion behavior and consequently dampen the corrosion rates at high pCO$_2$ conditions.
Modification in FeCO$_3$ Layer Formation and Growth Model

Solving equation (15) accounts several numerical issues. For example, the first term on the right hand side (RHS) of equation (15) is a hyperbolic equation with stiff non-linear source term. Furthermore, the second term on the RHS of equation (15) poses a convective-like effect in the equation. A convective term contributes to numerical instability in solving a partial differential equation, which includes incorrect front propagation and severe limit on time step. The numerical instability is more pronounced at high pCO$_2$ conditions. Thus in the present study, to minimize numerical instability, the hyperbolic precipitation rate equation was solved implicitly using exact analytical solution and front tracking scheme ($\varepsilon_i^{n+1} = \varepsilon_i^{n-1}$) was implemented for the convective component.

Equation (15) is solved in the 1D domain as shown in Figure 5. At the FeCO$_3$ layer/metal surface interface, the porosity is considered to be 1, as the corrosion process continuously creates voids underneath the FeCO$_3$ layer. At the other boundary (between the diffusion boundary layer and the bulk solution), it is assumed that no FeCO$_3$ can grow onto the boundary and out of the domain; therefore, porosity of FeCO$_3$ maintains at 1.

\[ \varepsilon = 1 \]

Bulk solution

\[ \frac{\partial \varepsilon}{\partial t} = - \frac{M_{FeCO_3}}{\rho_{FeCO_3}} \frac{dF_{FeCO_3}}{dV} - CR \frac{\partial \varepsilon}{\partial x} \]

Diffusion boundary layer

Steel surface

\[ \varepsilon = 1 \]
**Parametric Study**

Figure 6 shows the effect of pCO$_2$ on corrosion rate from model prediction for different pH values at 80°C. It is seen that the corrosion rate increases with increasing pCO$_2$ for both pH values. Figure 7 shows the effect of temperature on corrosion rate at 12 MPa of pCO$_2$. The corrosion rate increases with the increase in temperature due to the higher reaction rate at higher temperature. It is also observed that the corrosion rate changed greatly from 50°C to 80°C. Figure 8 represents the effect of pH on corrosion rate at 12 MPa of pCO$_2$ and 80°C. The corrosion rate slightly decreases from pH 3 to 5 and then it decreases to very low corrosion rate at pH 6 due to the formation of protective FeCO$_3$. Figure 9 shows the effect of flow velocity on corrosion rate for different temperatures at 12 MPa of pCO$_2$ and pH 3. It is observed that the increase in flow velocity accelerates the corrosion reaction at higher temperature (80°C).

![Graph showing the effect of pCO$_2$ on corrosion rate at different pH values (80°C and 1 m/s flow velocity).](image1)

**Figure 6:** Effect of pCO$_2$ on corrosion rate at different pH values (80°C and 1 m/s flow velocity).

![Graph showing the effect of temperature on corrosion rate at pH 3 (12 MPa pCO$_2$ and 1 m/s flow velocity).](image2)

**Figure 7:** Effect of temperature on corrosion rate at pH 3 (12 MPa pCO$_2$ and 1 m/s flow velocity).
Model Validation

The comparison between experimental data (obtained from autoclave and high pressure flow loop experiments)\textsuperscript{25-27} and model prediction is shown in Figure 10 under different combinations of pressure and temperature. The predicted corrosion rates show a good agreement with experimental data. Many similar comparisons were made for other conditions covered in this study, with similar results.
Figure 10: Comparison of corrosion rates between experiments and predictions in CO₂ environments at different conditions: (a) 0.3 ~ 2 MPa CO₂, 60°C, pH 5, (b) 8 MPa CO₂, 25°C ~ 80°C, pH 3.1 ~ 3.2, (c) 1 MPa ~ 14 MPa CO₂, 80°C, pH 3.1 ~ 3.4.

CONCLUSIONS

A predictive model was developed for corrosion of carbon steel in high pCO₂ conditions by modifying the existing CO₂ corrosion model for low pCO₂. The following conclusions are drawn:

- Water chemistry model was changed by considering non-ideality of the CO₂ phase.
- Electrochemical model was updated by including the Langmuir adsorption isotherm for H₂CO₃.
- FeCO₃ formation and growth model was improved by implementing front tracking scheme and exact analytical solution in order to avoid numerical instability.
- Corrosion rates predicted by the updated model showed a good agreement with experimental data under various high pCO₂ conditions.

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