CORROSION BEHAVIOR OF CARBON STEEL IN SUPERCritical CO₂ – WATER ENVIRONMENTS

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ABSTRACT

The corrosion behavior of carbon steel was investigated under supercritical CO₂ (scCO₂) – water systems to simulate the condition of CO₂ transportation pipeline in the CO₂ sequestration applications. To understand the thermodynamic properties of scCO₂-water systems related to the corrosion phenomena, thermodynamic modeling were conducted to determine the mutual solubilities of CO₂ and water in the two coexisting phases, and to calculate the concentrations of corrosive species in the free water at various pressures and temperatures. Carbon steel samples were exposed to water-saturated CO₂, and CO₂-saturated water in the pressure range of 40 to 80 bar at 50°C. The corrosion rate of samples was determined by weight loss measurements. The surface morphology and the composition of the corrosion product layers were analyzed by using surface analytical techniques (SEM and EDS).

Keywords: supercritical CO₂, thermodynamic modeling, CO₂ corrosion, carbon steel

INTRODUCTION

Emissions from fossil fuel-fired power plants represent a significant source of carbon dioxide (CO₂) emissions, a known greenhouse gas. The capture and storage of CO₂ in geological reservoirs is now considered to be one of the main options for achieving deep reductions in greenhouse gas emissions.¹,² The CO₂ capture and storage process involves three stages: capture of the CO₂ from the power plant or industrial process, transmission of the CO₂ to the storage site followed by injection into the geological reservoir.³ In order to avoid two-phase flow regimes and increase the density of the CO₂, the captured CO₂ gas is typically compressed to the supercritical state while the temperature and the pressure are over 31.1°C and 73.8 bar, respectively, thereby making it easier and less costly to transport.³,⁴ The research activities are largely concentrating on development of the capture technology to reduce costs, and on assessing the technical feasibility of injecting and monitoring the CO₂.
within the geological reservoirs themselves. Little of the research is being conducted on CO₂ transmission, but this remains a critical component that should not be overlooked.

Low alloy carbon steel pipelines have been used for transportation of CO₂ at high pressure, but in all cases, CO₂ must be dried to eliminate the corrosion risk. However, if CO₂ transport is to be achieved at a large scale or in existing pipelines, it will not be practical to dry it sufficiently and liquid water “breakout” is to be expected. Furthermore, drying CO₂ contributes to an increase in handling cost, especially for offshore installations where weight allowance and space for process equipment installation are very restricted. When free water exists in the pipeline, it will be saturated with CO₂ and the corrosion rate will be significant for carbon steel because of the formation of carbonic acid (H₂CO₃). In addition, even though pure, dry supercritical CO₂ is not corrosive, there are several studies which provide qualitative evidence for corrosion on carbon steel in water-saturated supercritical CO₂ phase. Thus, to be able to consider the corrosion risk in such pipelines, quantitative evaluation of corrosion in both CO₂-saturated water and water-saturated CO₂ phases will be needed.

The impact of CO₂ corrosion on carbon steel has been studied extensively at pressures relevant for oil and gas transport (up to 20 bar CO₂). At higher pressures experimental data are sparse. Since CO₂ changes from gaseous to liquid or supercritical with increasing pressure, it will lead to different interaction with water, i.e. CO₂ solubility in water will not follow Henry's law in liquid or supercritical CO₂ conditions, which results in changing water chemistry. Since the solubility of water in CO₂ is related to the free–liquid water formation and the solubility of CO₂ in water correlates with the corrosive potential of free water, accurate estimations of the mutual solubilities of CO₂ and water are important issue in the CO₂ transportation pipeline corrosion. Although many studies have been done to model mutual solubilities of CO₂ and water at high pressures, there is no attempt to predict the water chemistry at such a high pressure.

Thus, in the present study, to understand the thermodynamic properties of CO₂-water systems related to the corrosion phenomena, thermodynamic modeling were conducted to determine the mutual solubilities of CO₂ and water in the two coexisting phases, and to calculate the concentrations of corrosive species in the free–liquid water at various ranges of pressure and temperature (up to 300 bar, 85°C). In addition, the corrosion properties with increasing pressure were investigated for carbon steel by weight loss measurements and surface analysis techniques.

THERMODYNAMIC MODELING

The thermodynamic model used in this work was based on a combination of Spycher model (mutual solubilities of CO₂ and water) and Nesic model (chemistry of water-rich phase).

Modeling for mutual solubilities of CO₂-water system

Spycher et al. reviewed the published experimental P-T-x data for CO₂-water system in the temperature range of 12~100°C and pressure up to 600 bar to develop a solubility model. They used non-iterative procedure to calculate the composition of the compressed CO₂ and liquid phase at equilibrium based on equating chemical potentials and using the Redlich-Kwong (RK) equation of state (EOS). Their procedure is kept as simple as possible and is suitable for our purpose to establish a preliminary thermodynamic model to predict the mutual
solubilities of CO$_2$ and water in high pressure CO$_2$ pipeline applications. In the following, an approach for calculating the mutual solubilities of CO$_2$ and water is presented using the Spycher model.

At equilibrium of CO$_2$-water system, the following equilibrium relationship can be written:

\[
\begin{align*}
\text{H}_2\text{O}(g) & \rightleftharpoons \text{H}_2\text{O}(l) \quad (1) \\
K_{\text{H}_2\text{O}} &= f_{\text{H}_2\text{O}(g)}/a_{\text{H}_2\text{O}(l)} \quad (2) \\
\text{CO}_2(g) & \rightleftharpoons \text{CO}_2(aq) \quad (3) \\
K_{\text{CO}_2} &= f_{\text{CO}_2(g)}/a_{\text{CO}_2(aq)} \quad (4)
\end{align*}
\]

where $K$ is true equilibrium constants, $f$ is fugacity of the gas components, and $a$ is activity of components in the liquid phase. The $K$ values for water and CO$_2$ are functions of pressure and temperature as:

\[
K_{(T,P)} = K_{(T,P_0)}^0 \exp \left( \frac{(P-P_0)V_i}{RT} \right) \quad (5)
\]

where $P, P_0, R, T$ are pressure, reference pressure (1 bar), gas constant and temperature in K, respectively. $V_i$ is the average partial molar volume of the pure component $i$ over the pressure interval $P_0$ to $P$.

From the definition of fugacity ($f_i = \partial_i y_i P$)\textsuperscript{13}, the mole fraction of water in the CO$_2$ phase ($y_{\text{H}_2\text{O}}$) can be written with combining equation (2) and (5):

\[
y_{\text{H}_2\text{O}} = \frac{K_{\text{H}_2\text{O}}^0 a_{\text{H}_2\text{O}}}{\phi_{\text{H}_2\text{O}} P} \exp \left( \frac{(P-P_0)V_{\text{H}_2\text{O}}}{RT} \right) \quad (6)
\]

where, $\phi_{\text{H}_2\text{O}}$ is the fugacity coefficient of water.

For better accuracy at high pressures, the water activity deviation from unity caused by dissolved CO$_2$ should be taken into account. Using Raoult’s law, the water activity can be approximated by its mole fraction in the water phase ($x_{\text{H}_2\text{O}} = 1 - x_{\text{CO}_2}$), such that:

\[
y_{\text{H}_2\text{O}} = \frac{K_{\text{H}_2\text{O}}^0 (1-x_{\text{CO}_2})}{\phi_{\text{H}_2\text{O}} P} \exp \left( \frac{(P-P_0)V_{\text{H}_2\text{O}}}{RT} \right) \quad (7)
\]

where, $x_{\text{CO}_2}$ is the mole fraction of CO$_2$ in water phase. There is following relationship between $a_{\text{CO}_2}$ and $x_{\text{CO}_2}$:

\[
a_{\text{CO}_2} = 55.508 x_{\text{CO}_2} \quad (8)
\]

Substituting equation (5) and (8) into equation (4) gives:

\[
x_{\text{CO}_2} = \frac{\phi_{\text{CO}_2}(1-y_{\text{H}_2\text{O}})P}{55.508 K_{\text{CO}_2(g)}^0} \exp \left( - \frac{(P-P_0)V_{\text{CO}_2}}{RT} \right) \quad (9)
\]
Equations (7) and (9) can be solved directly by setting:

\[
A = \frac{K^0_{H_2O}}{\phi_{H_2O} P_{H_2O}^{P_{tot}}} \exp\left(\frac{(P-P^0)\bar{V}_{H_2O}}{RT}\right) \quad (10)
\]

\[
B = \frac{\phi_{CO_2} P_{CO_2}^{P_{tot}}}{55.508 K_{CO_2(g)}^{0}} \exp\left(-\frac{(P-P^0)\bar{V}_{CO_2}}{RT}\right) \quad (11)
\]

Using parameters A and B, we can calculate the mole fraction of water in the CO\(_2\) phase (\(y_{H_2O}\)) and the mole fraction of CO\(_2\) in the water phase (\(x_{CO_2}\)) as follows:

\[
y_{H_2O} = \frac{(1-B)}{A-B} \quad (12)
\]

\[
x_{CO_2} = B(1-y_{H_2O}) \quad (13)
\]

The average partial molar volume of the pure water (\(\bar{V}_{H_2O} = 18.1 \text{ cm}^3/\text{mol}\)) and CO\(_2\) (\(\bar{V}_{CO_2(g)} = 32.6 \text{ cm}^3/\text{mol}, \bar{V}_{CO_2(l)} = 32 \text{ cm}^3/\text{mol}\)), and the K parameters were obtained from the literature and/or by calibration to the solubility data:

\[
\log K^0_{H_2O} = -2.209 + 3.097 \times 10^{-2}T - 1.098 \times 10^{-4}T^2 + 2.048 \times 10^{-7}T^3 \quad (14)
\]

\[
\log K^0_{CO_2(g)} = 1.189 + 1.304 \times 10^{-2}T - 5.446 \times 10^{-5}T^2 \quad (15)
\]

\[
\log K^0_{CO_2(l)} = 1.169 + 1.368 \times 10^{-2}T - 5.380 \times 10^{-5}T^2 \quad (16)
\]

where T is temperature in °C.

The fugacity coefficients in equations (10) and (11) should be derived from an equation of state (EOS) which can calculate properties of CO\(_2\)-water mixtures. In this study, Redlich-Kwong (RK) EOS was used to get the fugacity coefficients and the volume of the compressed gas phase. The RK EOS is given by\(^{12}\):

\[
P = \left(\frac{RT}{\bar{V}}\right) - \left(\frac{a}{\bar{V}^{0.5}(\bar{V}+b)}\right) \quad (17)
\]

where \(\bar{V}\) is the molar volume of the CO\(_2\)-rich phase at pressure P and temperature T, and R is the gas constant. Parameters a and b characterize intermolecular attraction and repulsion, respectively.

For CO\(_2\)-water mixtures, the mixture constants \(a_{mix}\) and \(b_{mix}\) can be calculated by the standard mixing rules:

\[
a_{mix} = \sum_{i=1}^{n} \sum_{j=1}^{n} y_i y_j a_{ij} = y_{H_2O}^2 a_{H_2O} + 2y_{H_2O} y_{CO_2} a_{H_2O-CO_2} + y_{CO_2}^2 a_{CO_2} \quad (18)
\]

\[
b_{mix} = \sum_{i=1}^{n} y_i b_i = y_{H_2O} b_{H_2O} + y_{CO_2} b_{CO_2} \quad (19)
\]

From these mixing rules and equation (17), the fugacity coefficient of component k in mixture with other component i can be calculated as:
\[ \ln(\phi_k) = \ln \left( \frac{V}{V_{b_{\text{mix}}}} \right) + \left( \frac{b_k}{V_{b_{\text{mix}}}} \right) \ln \left( \frac{V^{+b_{\text{mix}}}}{V} \right) + \left( \frac{a_{\text{mix}}b_k}{RT^{1.5}b_{\text{mix}}} \right) \ln \left( \frac{V^{+b_{\text{mix}}}}{V+b_{\text{mix}}} \right) - \ln \left( \frac{PV}{RT} \right) \quad (20) \]

To avoid an iterative scheme, the assumption of infinite water dilution in the CO\(_2\)-rich phase is made that \( y_{H_2O} = 0 \) and \( y_{CO_2} = 1 \) in the mixing rules in equation (18) and (19). Then, \( a_{\text{mix}} \) and \( b_{\text{mix}} \) can be replaced to \( a_{CO_2} \) and \( b_{CO_2} \) in equation (20), respectively. And the volume of the compressed gas phase (V) can be calculated by recasting RK EOS in terms of volume:

\[ V^3 - V^2 \left( \frac{RT}{P} \right) - V \left( \frac{RT b_{CO_2}}{P} - a_{CO_2} \right) \frac{p}{T^{0.5}} + b_{CO_2}^2 = 0 \quad (21) \]

where, \( R = 83.1447 \text{ barcm}^3\text{mol}^{-1}\text{K}^{-1} \), \( V \) is in \text{cm}^3/mol, \( P \) is in bar, and \( T \) is in K.

A FORTRAN program was used to calculate the mutual solubilities of \( CO_2 \) and water in the temperature range of 15~85°C and pressure up to 300 bar.

**Modeling for the chemistry of free water and for the prediction of FeCO\(_3\) precipitation**

Understanding water chemistry is an important precondition for predicting corrosion under high \( CO_2 \) pressure. The concentrations of carbonic species (\( CO_2(\text{aq}), H_2CO_3, HCO_3^- \), and \( CO_3^{2-} \)) as well as pH in the water phase were calculated to provide a tool for estimating water chemistry of a pipeline when water precipitates using the solubility of \( CO_2 \) and equilibrium constants for each chemical reaction at various pressure and temperature ranges. In the case of \( CO_2 \) transporting pipelines, due to a virtually unlimited supply of \( CO_2 \), there is constant partial pressure of \( CO_2 \) on the surface of free water so that the system can be considered as an ‘open’ system.

Once \( CO_2 \) dissolves in water (equation (3)), \( CO_2(\text{aq}) \) is involved in a sequence of chemical reactions as follows:

\[
\begin{align*}
CO_2(\text{aq}) + H_2O & \underset{K_{\text{hyd}}}{\leftrightarrow} H_2CO_3 \quad \text{(Hydration of aqueous \( CO_2 \))} \\
H_2CO_3 & \underset{K_{\text{ca}}}{\leftrightarrow} H^+ + HCO_3^- \quad \text{(Dissociation of carbonic acid)} \quad (22) \\
HCO_3^- & \underset{K_{\text{ki}}}{\leftrightarrow} H^+ + CO_3^{2-} \quad \text{(Dissociation of bicarbonate ion)} \quad (24) \\
H_2O & \underset{K_{\text{kw}}}{\leftrightarrow} H^+ + OH^- \quad \text{(Dissociation of water)} \quad (25)
\end{align*}
\]

With the partial pressure of \( CO_2 \) known in an open system, Henry’s law can be applied in order to calculate the vapor-liquid equilibrium of \( CO_2 \) at low pressure.\(^1\) However, at high pressure, Henry’s law can’t be used to calculate the concentration of \( CO_2 \) in the solution. Thus, in the present study, the concentrations of \( CO_2 \) in the water (\( C_{CO_2} \)) were calculated using the solubility of \( CO_2 \) in water (\( x_{CO_2} \)) obtained from equation (13).

Once concentration of dissolved \( CO_2 \) is fixed, the reactions shown above can be described by equilibria reactions as follows based on the assumption of infinite dilution:

\[ K_{\text{hyd}} = \frac{C_{H_2CO_3}}{C_{CO_2} C_{H_2O}} \quad (26) \]
\[
K_{ca} = \frac{C_{\text{H}^+} C_{\text{HCO}_3^-}}{C_{\text{H}_2\text{CO}_3}} \quad (27)
\]
\[
K_{bi} = \frac{C_{\text{H}^+} C_{\text{CO}_3^{2-}}}{C_{\text{HCO}_3^-}} \quad (28)
\]
\[
K_w = \frac{C_{\text{H}^+} C_{\text{OH}^-}}{C_{\text{H}_2\text{O}}} \quad (29)
\]

where \(C_{\text{H}_2\text{CO}_3}, C_{\text{HCO}_3^-}, C_{\text{CO}_3^{2-}}, C_{\text{H}^+}, \) and \(C_{\text{OH}^-}\) are the concentrations (mol/L) of 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:

\[
C_{\text{H}^+} = C_{\text{HCO}_3^-} + 2 \times C_{\text{CO}_3^{2-}} + C_{\text{OH}^-} \quad (30)
\]

Supersaturation (SS) of iron carbonate is calculated using the following equation:\textsuperscript{15,16}

\[
SS = \frac{C_{\text{Fe}^{2+}} C_{\text{CO}_3^{2-}}}{K_{sp}} \quad (31)
\]

where \(C_{\text{Fe}^{2+}}\) is the concentration of ferrous ion in the solution, and \(K_{sp}\) is the solubility limit of iron carbonate. The scale will precipitate when the SS value exceeds unity i.e. when the solution is supersaturated. From the literature review, it is found that the Greenberg and Tomson equation\textsuperscript{17} is the best choice for describing iron carbonate solubility limit as a function of temperature. It should be noted that Greenberg and Tomson’s experiments used a de-ionized water solution and assumed that ionic strength is 0. However, it can be calculated that the ionic strength was actually 0.002 because of the other ions present in the solution, such as \(\text{H}^+, \text{HCO}_3^-, \text{CO}_3^{2-}, \) and \(\text{OH}^+, \text{Fe}^{2+}\). When this is accounted for, a slightly revised equation is obtained:\textsuperscript{15}

\[
\log K_{sp} = -59.3498 - 0.041377 T_K \frac{2.1963}{T_K} + 24.5724 \log(T_K) \quad (32)
\]

A FORTRAN and excel programs were used to calculate the concentrations of species in the solution and the precipitation of iron carbonate with various temperature and pressure ranges.

**EXPERIMENTAL PROCEDURE**

The test specimens were machined from X65 low carbon steel with a size of 25 X 15 X 3 mm. The composition of this steel is given in Table 1. The specimens were ground with 600 grit silicon carbide paper, cleaned with alcohol in ultrasonic bath, dried, and weighed using a balance with a precision of 0.1 mg. The electrolyte used in this work was 1 wt.% NaCl solution.
The weight loss experiments were performed in a 2000 psi static autoclave with 1000 ml volume (Figure 1). 400 ml of solution was added to the autoclave and CO\textsubscript{2} gas was bubbled for 3 h to remove oxygen before starting the test. Corrosion tests were conducted under different pressures (40 ~ 80 bar) at 50\textdegree{}C. When both water and CO\textsubscript{2} are added in the autoclave, there is a phase separation with the water phase at the bottom. Corrosion coupons were inserted both in the water-saturated CO\textsubscript{2} phase at the top of the autoclave and in the CO\textsubscript{2}-saturated water phase at the bottom.

The corrosion rates were determined from weight-loss method at the end of a 24-hour exposure. The specimens were removed and cleaned for 5 min in the Clarke’s solution (20 g antimony trioxide + 50 g stannous chloride and hydrochloric acid to make 1000 ml). The specimens were then rinsed in distilled water, dried and weighed to 0.1 mg. The corrosion rate can be calculated by the following equation\textsuperscript{18}:

\[
\text{Corrosion rate (mm/y)} = \frac{8.76 \times 10^4 \times \text{weight loss (g)}}{\text{area (cm}^2\text{)} \times \text{density (g/cm}^3\text{)} \times \text{time (hour)}}
\] (33)

The morphology and compositions of corrosion products were analyzed by SEM and EDS.

RESULTS

Thermodynamic modeling

The mutual solubilities of CO\textsubscript{2} and water calculated using equations (12) and (13) are shown in Figures 2 and 3 in terms of mole fractions of water and CO\textsubscript{2}. The solubility of water in CO\textsubscript{2} showed high values at low pressures, passes through a minimum, and then increased with pressure. The discontinuity in water solubility at subcritical temperatures (15, 25\textdegree{}C) coincides with the phase change from a gaseous to a liquid CO\textsubscript{2}. Above the critical temperature (31.1\textdegree{}C), it is related to the phase change from a gaseous to a supercritical CO\textsubscript{2} after which trend with pressure becomes smoother. However, the solubility of CO\textsubscript{2} in water increased sharply with rising pressure up to the saturation pressure and at a lesser rate thereafter. The CO\textsubscript{2} solubility trend with pressure reflected two solubility curves for two distinct phases: liquid or supercritical CO\textsubscript{2} above saturation pressure, and gaseous CO\textsubscript{2} below this pressure. This resulted in a break in slope on the overall solubility trends.

Furthermore, as shown in Figures 2 and 3, the CO\textsubscript{2}-water system is highly asymmetric: solubility of water in CO\textsubscript{2} is smaller than that of CO\textsubscript{2} in water by one order of magnitude. This is due to the property difference of molecular CO\textsubscript{2} and water.\textsuperscript{19} CO\textsubscript{2} is a non-polar molecule and the key intermolecular force is the London force, while water is a strong polar molecule and intermolecular interaction depends primarily on hydrogen bonds. In the CO\textsubscript{2}-water binary mixture, molecular interactions between two like molecules are much stronger than those between two unlike molecules (water and CO\textsubscript{2}). This dissimilarity results in the low solubility of water in the CO\textsubscript{2}-rich phase. The electrostatic forces of water molecules can polarize CO\textsubscript{2} molecules, and then increase their ability to penetrate the water phase; consequently, the solubility of CO\textsubscript{2} in water is much larger than that of water in CO\textsubscript{2}. Since the amount of water in CO\textsubscript{2} is quite small, such that the CO\textsubscript{2} properties (density, conductivity) can be approximated fairly well by those of pure CO\textsubscript{2}.
The effects of temperature on the solubility of water and on the solubility of CO2 are significantly different, and the solubility of water increased while the solubility of CO2 decreased with increase in temperature. This behavior of the CO2-water system is due probably to changes in compressibility of CO2 and hydration of water\textsuperscript{20}; e.g., at 80 bar the density of CO2 is 707.2 kg/m\textsuperscript{3} at T=30°C and becomes 966 kg/m\textsuperscript{3} at T=0°C, indicating that the resistance for water to penetrate into CO2 decreases with increase temperature; in comparison, water density varies with temperature only slightly, and the effect of hydration, which enhance the dissolution of CO2 in water is greater at low temperature than at high temperatures.

Figure 4 shows a comparison between the predicted solubility of water in CO2 and that from experimental data available in the literature\textsuperscript{21-26} The comparison demonstrates an acceptable match in the temperature range of 15~50°C, however, calculated water solubility has less accurate at higher temperatures, because the water mole fractions in the CO2 phase keeps increasing with temperature so that the assumption of infinite water dilution should eventually breakdown. A comparison between solubility of CO2 in water calculated using the model versus the experimental data\textsuperscript{21-26} is represented in Figure 5. Results presented in Figure 5 show a good agreement at various temperatures and pressures.

The effects of pressure and temperature on the concentrations of carbonic species (H\textsubscript{2}CO\textsubscript{3}, HCO\textsubscript{3}\textsuperscript{-}, and CO\textsubscript{3}\textsuperscript{2-}) and pH (H\textsuperscript{+}) are shown in Figures 6 and 7. The concentrations of H\textsubscript{2}CO\textsubscript{3} and HCO\textsubscript{3}\textsuperscript{-} showed a same trend as the solubility of CO2 in water shown in Figure 3, i.e., the concentrations increased with increasing pressure whereas decreased with temperature. However, the concentration of CO\textsubscript{3}\textsuperscript{2-} increased with increasing pressure and temperature. The pH value changed in the range of 4.4 to 3 which decreased with an increase in pressure and increased with increasing temperature. The pH of free water will be in the range of 3.1 ~ 3.3 under supercritical CO\textsubscript{2} condition (P>73 bar, T>31.1°C), which can lead more acidic environment compare with atmospheric condition (pH 3.9 at 1 bar, 25°C). At this low pH values, the solubility of iron carbonate is sufficiently high that no precipitate would be observed (scale-free CO\textsubscript{2} corrosion).

**Corrosion tests under supercritical CO\textsubscript{2}-water system**

Figure 8 shows the corrosion rate of carbon steel under different pressures at 50°C. Note that the CO\textsubscript{2} phase was gaseous at 40 and 60 bar, whereas it was supercritical at 80 bar. Corrosion coupons in the CO\textsubscript{2}-rich phase did not show any visible corrosion attack, and low corrosion rates were measured. As shown in Figure 8, the corrosion rates in CO\textsubscript{2}-saturated water phase are much higher than in water-saturated CO\textsubscript{2} phase. However, there is little difference in the corrosion rate with pressure in CO\textsubscript{2}-saturated water phase. Based on the water chemistry predicted in Figure 7 (b), the pH in these experiments would be 3.25 (40 bar), 3.18 (60 bar), and 3.14 (80 bar), which suggests an iron carbonate scale-free CO\textsubscript{2} corrosion. At pH 4 or below, direct reduction of H\textsuperscript{+} ions (2H\textsuperscript{+} + 2e\textsuperscript{-} → H\textsubscript{2}) is important and the pH has a direct effect on the corrosion rate.\textsuperscript{27} However, the most important effect of pH is indirect and relates to how pH changes conditions for formation of iron carbonate scales. High pH results in a decreased solubility of iron carbonate and leads to an increased precipitation rate and higher scaling tendency. To predict this, the degree of saturation for iron carbonate as a function of pressure at 50°C with different ferrous ion concentrations and pH are shown in Figures 9 and 10. The ferrous ion concentrations were selected based on the results of the corrosion tests. It has been found that under test conditions (40 ~ 80 bar) iron carbonate is under-saturated
when pH is 3 and supersaturated when pH is 4 with more than 200 ppm of the ferrous ion concentration.

Figures 11 and 12 show the surface morphologies of the corroded samples at different pressures before and after cleaning with the Clarke’s solution. The analysis by SEM and EDS revealed that the morphologies were almost identical with pressure, and the surface was locally covered by the corrosion products (FeCO$_3$). This indicates that iron dissolution reaction proceeds with time and leads to an increase in pH at the steel surface by accumulating dissolved ferrous ions, and then iron carbonate precipitate due to the local supersaturation. However, as shown in Figure 8, corrosion rates did not change much with pressure, even if some iron carbonate precipitation occurs, reflecting the fact that a relatively porous, detached and unprotective scale was formed. In addition, after removing these corrosion products, a severe uniform corrosion attack for all samples was revealed (Figure 12).

CONCLUSIONS

The mutual solubilities of CO$_2$ and water, and the chemistry of the free water in a wide temperature and pressure ranges were predicted by thermodynamic modeling works. In addition, the corrosion properties with increasing pressure were investigated for carbon steel by weight loss measurements and surface analysis techniques. The following conclusions are drawn:

- The solubility of water in CO$_2$ and the solubility of CO$_2$ in water at supercritical CO$_2$ condition increased with increasing pressure, however, the solubility of CO$_2$ in water was much larger than that of water in CO$_2$.
- The solubility of water in CO$_2$ increased while the solubility of CO$_2$ in water decreased with increase in temperature.
- The calculated water solubility in CO$_2$ showed that the agreements between the calculation results and the experimental data were quite well at low and medium temperatures, and up to 300 bar of pressure. When temperature was above 75°C, there were remarkable discrepancies.
- The calculated CO$_2$ solubility in water from 15 to 85°C, and up to 300 bar showed a good agreement with experimental data.
- The concentrations of CO$_2$(aq), H$_2$CO$_3$ and HCO$_3^-$ increased with increasing pressure but decreased with an increase in temperature. The concentration of CO$_3^{2-}$ increased linearly with increasing pressure and temperature, and the pH value changed in the range of 4.4 to 3 which decreased with an increase in pressure and increased with increasing temperature.
- Corrosion coupons in the CO$_2$-rich phase did not show any significant corrosion attack, and low corrosion rates were obtained.
- The corrosion rates of carbon steel in CO$_2$-saturated water were very high but did not change much with pressure from 40 to 80 bar.

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TABLE 1
ELEMENT ANALYSIS FOR THE X65 CARBON STEEL USED IN THE TESTS (WT %)

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Cu</th>
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<td>C</td>
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<td>0.25</td>
<td>0.013</td>
<td>0.001</td>
<td>0.05</td>
<td>0.04</td>
<td>0.04</td>
<td>0.007</td>
<td>0.041</td>
</tr>
</tbody>
</table>

FIGURE 1 – The Test Autoclave Used for Corrosion Experiments
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FIGURE 3 – Solubility of CO₂ in Water as Functions of Pressure and Temperature
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