

Effect of Acetic Acid on Corrosion Product Layer Formation in Aqueous CO₂ Environments

Sahithi Ayyagari, Bruce Brown, Srdjan Nesic
Institute for Corrosion and Multiphase Technology, Ohio University
342 W State Street
Athens, Ohio, 45701
USA

ABSTRACT

The effect of the presence of acetic acid (HAc) on the formation of corrosion product layers in aqueous CO₂ environments was investigated using electrochemistry, weight loss, and extensive surface analysis procedures. Electrochemical tests (LPR, EIS, and potentiodynamic sweeps) were conducted in a 4 L glass cell with seven specimens of API 5L X65 steel - one for electrochemical measurements and six for surface analyses. Experiments were conducted in test solutions without organic acid and with 0.5 mM (30 ppm) undissociated HAc for ~240 h (10 days) and specimens were retrieved after 12 h, 120 h, and 240 h. The condition necessary for precipitation of iron carbonate, i.e., saturation level $S(\text{FeCO}_3) > 1$ was achieved by adding an external source of Fe²⁺ ions (de-oxygenated aqueous FeCl₂) at the beginning of the experiment. Modified thermodynamic calculations for the initial saturation value for iron carbonate, $S_{\text{in}}(\text{FeCO}_3)$, were used to compensate for complexation in experiments conducted in the presence of HAc. Surface and cross-sectional analysis were performed using XRD, SEM/EDS, and surface profilometry. It was observed that the corrosion product layers, formed without HAc and with 0.5 mM free HAc, remained protective, showing no indication of localized corrosion. The anodic and cathodic reactions of mild steel in solutions without HAc and with 0.5 mM free HAc were retarded by the formation of corrosion product layers indicating their protectiveness.

Key words: Complexation, acetic acid, CO₂ corrosion, localized corrosion, electrochemical measurements

INTRODUCTION

Several studies have focused in the past on the precipitation mechanism of iron carbonate (FeCO₃), which is the dominant corrosion product in CO₂ environments observed in the oil and gas industry. The dissolved CO₂ species undergo a series of chemical reactions and react with the oxidized iron ions forming FeCO₃ as the primary corrosion product. In the past, the thermodynamics of each of these reactions have been thoroughly studied and modified by incorporating the effects of temperature and non-ideality.

The overall precipitation/dissolution reaction of FeCO_3 can be written as follows:



Net precipitation of FeCO_3 is observed when the solution becomes supersaturated with FeCO_3 , i.e., when the solution exceeds the solubility limit of FeCO_3 . Saturation value can be calculated using the following expression:

$$S(\text{FeCO}_3) = \frac{[\text{Fe}^{2+}][\text{CO}_3^{2-}]}{K_{sp}} \quad (2)$$

where K_{sp} , the solubility product of iron carbonate, is a function of temperature (T) and solution ionic strength (I)^[1]:

$$K_{sp} = 10^{-\left(-59.4 - 0.041377T_K - \frac{2.1963}{T_K} + 24.5724 \log(T_K) + 2.6349I^{0.5} - 1.0027I\right)} \quad (3)$$

$$I = \frac{1}{2} \sum_i c_i z_i^2 \quad (4)$$

where c_i is the concentration of each species in solution and z_i is the charge of the species.

The addition of organic acids to a pure CO_2 system complicates the water chemistry by inducing a change in pH and ionic strength, and formation of soluble complexes. Formation of soluble acetate complexes decreases the concentration of Fe^{2+} ions freely available, which decreases the bulk $S(\text{FeCO}_3)$ in the solution^[2]. A previous study by Gulbrandsen et al.^[2] has shown that as long as the solution is supersaturated, i.e. $S(\text{FeCO}_3) > 1$, protective corrosion product layers are formed regardless of the presence of HAc. Similar results have been reported in other studies, wherein, the presence of HAc merely delayed the formation of a protective FeCO_3 layer^[3]. The feasibility and importance of formation of soluble acetate complexes, especially at higher temperatures, was explained in another study by Gulbrandsen et al.^[4]. It was suggested that the driving force required for the formation of protective FeCO_3 films may become lower due to the formation of complexes. Equations for thermodynamic equilibrium constants for ferrous acetate complexes were obtained experimentally from a potentiometric titration study^[5]; this previous study, conducted by Palmer et al.^[5], further emphasized the need to review the water chemistry calculation with the addition of equilibrium constants for ferrous acetate complexes to better determine the concentration of freely available Fe^{2+} ions, especially at higher temperatures and higher concentrations of HAc.

The presence of organic acids may lead to instability in the FeCO_3 layer because of the changes in water chemistry. The influence of temperature and ionic strength on bulk solution pH, $S(\text{FeCO}_3)$, and FeCO_3 layer formation has received attention, leading to modification of the expression for solubility product.^[1] However, despite the indications of the effects of complexation in the presence of organic acids, this effect has not been incorporated into corrosion product layer formation studies. This is an important area to focus upon in order to better understand the overall effect that organic acids have on the stability and formation of the FeCO_3 corrosion product layers.

In this context, thermodynamic calculations for corrosion product layer formation have been modified using equilibrium constants derived from Palmer et al.'s study^[5] to compensate for complexation in experiments conducted in the presence of HAc. The present study aimed at understanding the protectiveness of the FeCO_3 corrosion product layers over longer exposures and the effect of HAc.

EXPERIMENTAL

Equipment

Electrochemical tests were conducted in a 4-liter glass cell with seven specimens of API 5L X65 steel - one for electrochemical measurements and six for surface analyses. The corrosion specimens were flat, identical in size, with a working area of $\sim 1.45 \text{ cm}^2$, and were located at the same radial distance from the center of the glass cell. The electrochemical specimen had an electrical connection established by soldering a copper wire to the back of the specimen, while the other specimens were simply immersed in the test solution. **Error! Reference source not found.** shows different parts of the experimental setup.

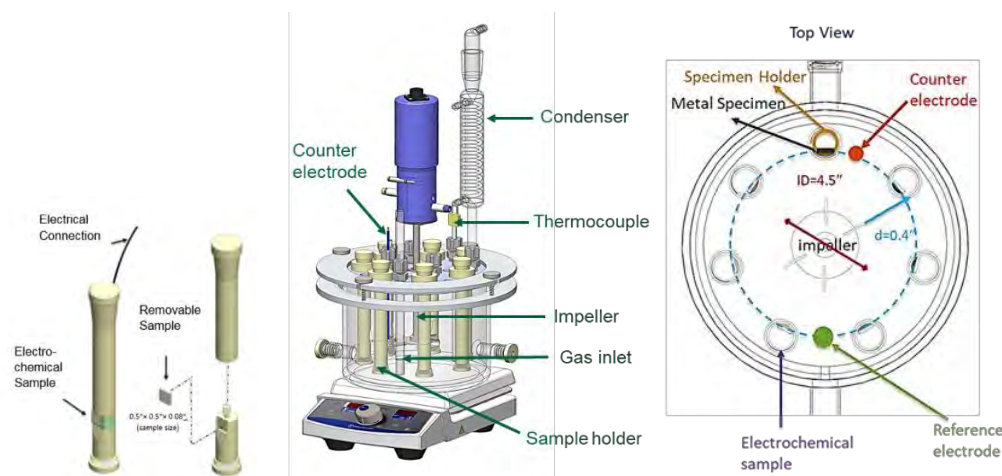


Figure 1. Experimental setup showing front view and top view of the glass cell

Test Matrix

Experiments were conducted in test solutions without organic acid and with 0.5 mM free HAc in a 1 wt.% NaCl solution de-aerated for at least 2 h with CO_2 sparging. The solution was continuously sparged with CO_2 and was maintained at 80°C and pH 6.6 throughout the duration of the experiment. The details of the test are shown in Table 1.

Table 1
Experimental parameters for layer forming conditions

Parameter	Conditions	
Temperature	$80 \pm 2^\circ\text{C}$	
pH	6.60 ± 0.02	
pCO_2	0.53 bar	
Electrolyte	1 wt.% NaCl	
Flow condition	Quiescent	
Specimen	X-65 flat specimens (1.45 cm^2)	
Measurements	EIS for solution resistance (R_s) LPR for polarization resistance (R_p) Potentiodynamic sweeps for corrosion mechanisms	
$S_{\text{in}}(\text{FeCO}_3)$	~ 150	
$[\text{Fe}^{2+}]_{\text{in}}$	25 ppm	32 ppm
Total organic acid	0	27.8 mM HAc (1668 ppm)
Free HAc	0	0.5 mM (30 ppm)

Calculations for concentration of acetate complexes

Dissociation of HAc:



$$K_{HAc} = 10^{-(-6.661 - 0.0135 \cdot T_K + 0.000238 \cdot (T_K)^2)} \quad (6)$$

Formation of FeAc⁺ [5]:



$$Q_1 = \frac{[FeAc^+]}{[Fe^{2+}][Ac^-]} \quad (8)$$

$$\log Q_1 = -\frac{4AI^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} - \frac{10693}{T_K} - 55.283 \ln(T_K) + 0.07924T_K + 328.05 - 10.384I + 0.010138T_K \\ + (5.4101 \times 10^{-4})I^2T_K + \frac{1426.8I^2}{T_K} + 13.706I \left\{ \frac{\left((1 + 2I^{\frac{1}{2}} - 2I) \exp(-2I^{\frac{1}{2}}) \right)}{4I} \right\} \quad (9)$$

Formation of FeAc₂ [5]:



$$Q_2 = \frac{[FeAc_2]}{[Fe^{2+}][Ac^-]^2} \quad (11)$$

$$\log Q_2 = -\frac{6AI^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} - \frac{24890}{T_K} - 135.86 \ln(T_K) + 0.19611T_K + 800.73 + \frac{435.0681I}{T_K} \\ - (3.1813 \times 10^{-3})I^2T_K + (4.9867 \times 10^{-6})T_K^2I \quad (12)$$

where, A is the Debye - Huckel parameter, and can be calculated as follows:

$$A = -2.97627 + 4.80688 \cdot 10^{-2}T_K - 2.6928 \cdot 10^{-4}T_K^2 + 7.49524 \cdot 10^{-7}T_K^3 - 1.02352 \cdot 10^{-4}T_K^4 \\ + 5.58004 \cdot 10^{-13}T_K^5 \quad (13)$$

The total [Fe²⁺] present in the solution were measured using a spectrophotometer. A part of this measured [Fe²⁺] exists as complexes in the presence of HAc. The concentration of these complexes can be calculated using the above-mentioned expressions. The effective [Fe²⁺] that is available for the formation of FeCO₃ can be thus calculated as follows:

$$[Fe^{2+}]_{free} = \Sigma[Fe^{2+}]_{total} - [FeAc^+] - [FeAc_2] \quad (14)$$

For the present experimental conditions with 0.5 mM undissociated HAc at 80°C and pH 6.60, 32 ppm of [Fe²⁺] was added initially. This corresponds to an initial saturation of ~200. However, 11.23% of the