

# A STUDY OF PROTECTIVE IRON CARBONATE SCALE FORMATION IN CO<sub>2</sub> CORROSION

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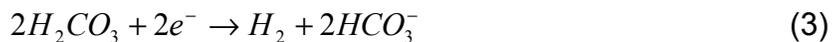
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## Introduction

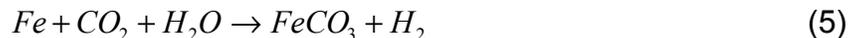
Iron carbonate scale that forms on mild steel in CO<sub>2</sub> environments is a frequent concern in the oil and gas production and transportation industry. Pure CO<sub>2</sub> corrosion can lead to serious internal corrosion of carbon steel. The anodic reaction on the steel surface is:



The cathodic reactions in CO<sub>2</sub> solutions are:



When the concentrations of Fe<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> ions exceed the solubility limit, solid iron carbonate precipitates on the steel surface. The overall reaction in the case of CO<sub>2</sub> corrosion is:



Iron carbonate scale formation is one of the most important factors governing the rate of corrosion. The iron carbonate film can slow the corrosion process by presenting a diffusion barrier for the species involved and by covering up a portion of the steel surface and preventing the underlying steel from further dissolution. Iron carbonate film growth depends primarily on the kinetics of scale formation (Johnson, 1991; Van Hunnik, 1996). As more iron carbonate precipitates, the film grows in density as well as thickness. However, the steel surface corrodes under the film, continuously creating a “void” between the film and the steel surface. When the rate of precipitation at the steel surface equals or exceeds the rate of corrosion, dense, protective films form—sometimes very thin but still protective. The opposite occurs when the corrosion process undermines the newly formed film faster than precipitation

can fill in the voids, and a porous and unprotective film forms which can be sometimes very thick. This investigation was conducted to elucidate the iron carbonate scale formation process in CO<sub>2</sub> corrosion.

## Experimental Methods

The experiments were performed in a glass cell as shown in Figure 1. The glass cell was filled with 2 liters of distilled water with 1 wt % NaCl. The solution was heated to 80°C and purged with CO<sub>2</sub> at 1 bar. After the solution was deoxygenated, the pH was increased from the equilibrium value of 4.18 to the desired value by adding a deoxygenated sodium bicarbonate solution. Later, the required amounts of Fe<sup>2+</sup> were added in the form of a deoxygenated ferrous chloride salt (FeCl<sub>2</sub>·4H<sub>2</sub>O) solution. The steel specimens were then inserted into the solution. Prior to immersion, the specimen surfaces were polished successively with 240, 400 and 600 grit SiC paper, rinsed with alcohol, and degreased using acetone. Both carbon steel (X-65) and stainless steel were used as the substrates to grow the iron carbonate scale.

Direct measurement of iron carbonate scale precipitation kinetics (weight gain/loss method) were developed to obtain the precipitation rate. The precipitation rate of iron carbonate film was obtained by weighing the coupons on which iron carbonate films were deposited before and after removing the films. The coupon with the iron carbonate scale on it was observed using Scanning Electron Microscopy (SEM). The inhibitors chosen were generic inhibitors of known formulation and were recommended by the consortium of companies sponsoring this research. They were provided to us by Champion Technologies, Inc.

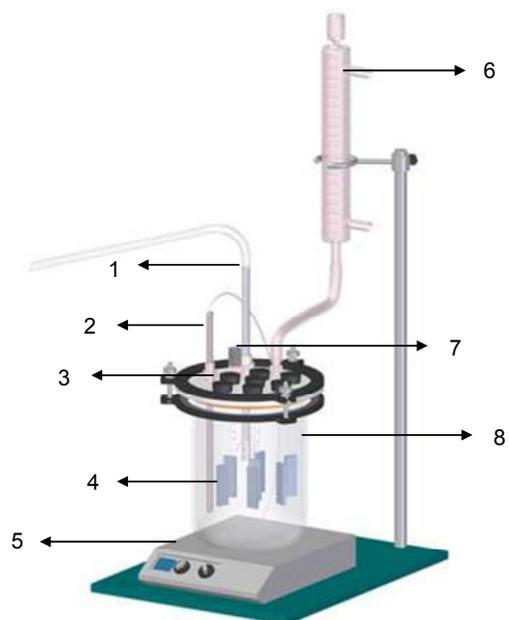


Figure 1. Schematic of the experimental test cell: 1. bubbler; 2. temperature probe; 3. rubber cork with nylon cord; 4. specimen; 5. hot plate; 6. condenser; 7. pH probe; 8. glass cell.

## Results and Discussion

Precipitation experiments were conducted in the stagnant solution under iron carbonate supersaturations of 7 to 150 and a temperature of 80°C. The precipitation rate of iron carbonate measured by weight gain/loss method shows good reproducibility, as illustrated in Figure 2. Error bar was obtained by finding the maximum and minimum values of the experiments. With the increase of supersaturation of iron carbonate, the precipitation rate increased. Discrepancies in measured precipitation rate were identified when compared to literature data which were traced back to the indirect experimental techniques used there to obtain the original precipitation kinetics data (Johnson and Tomson 1991 and Van Hunnik 1996). New data generated in the present project are one to two orders of magnitude lower compared to the ones obtained by those authors, as shown in Figure 3.

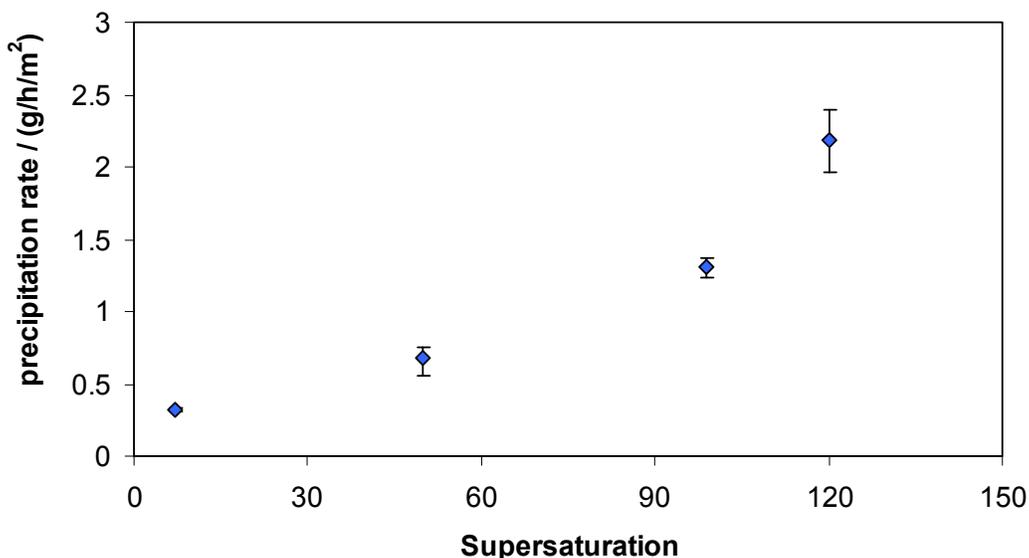
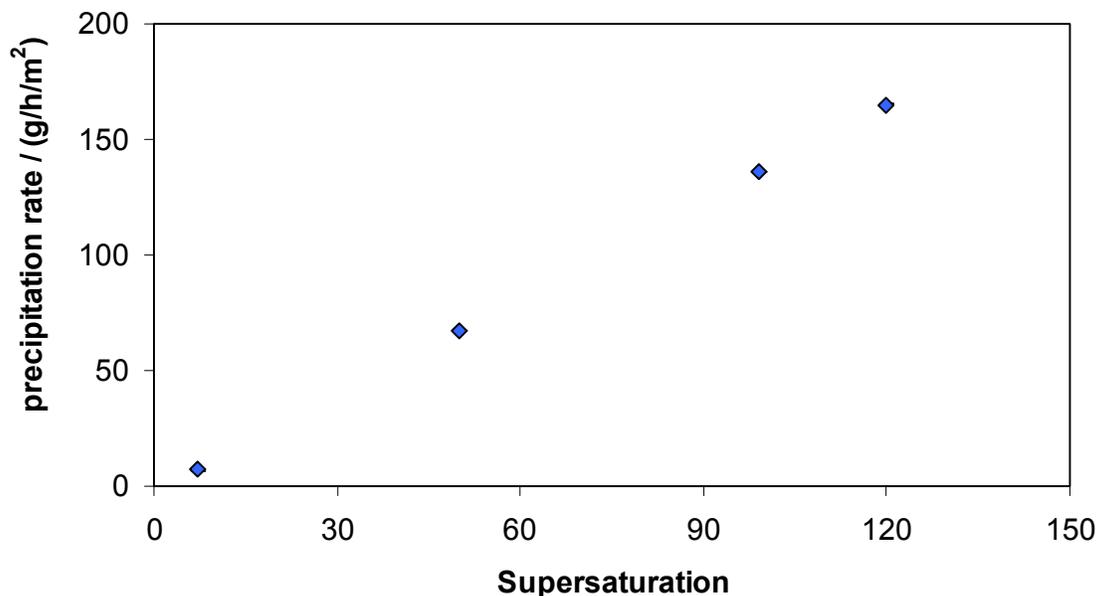
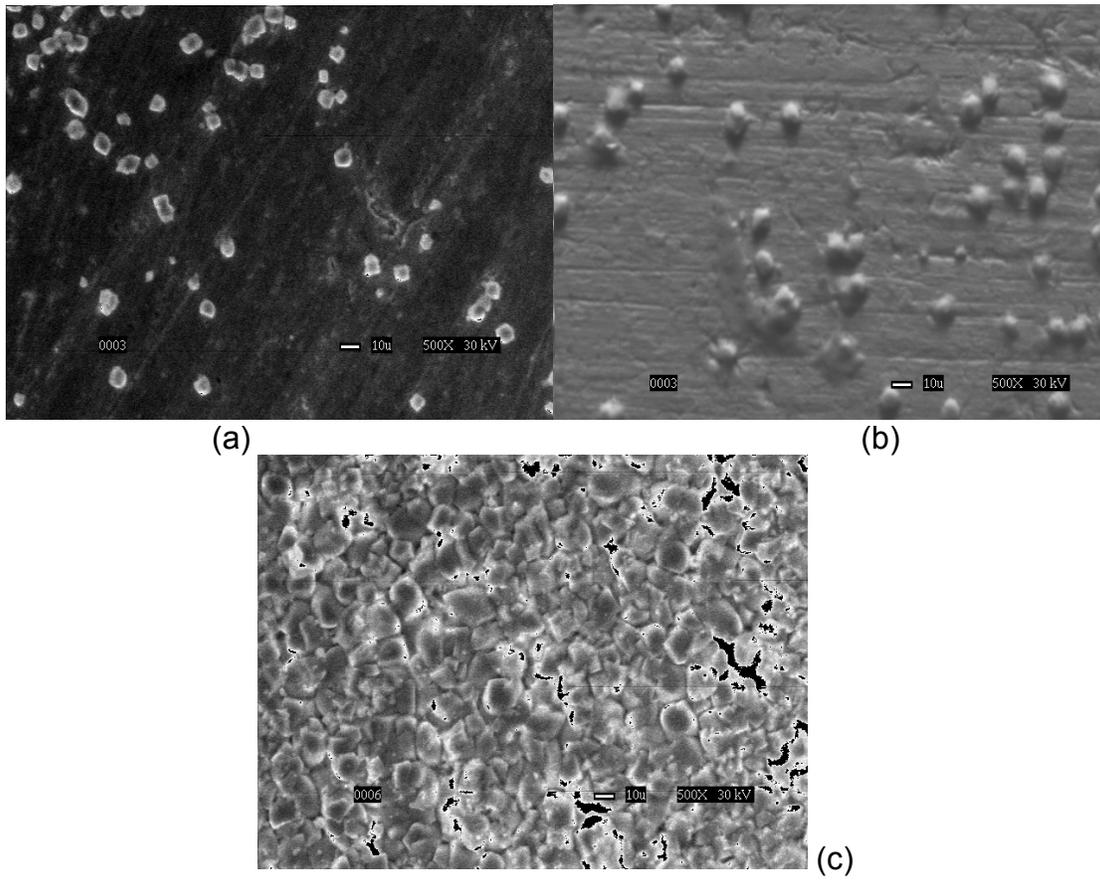


Figure 2. Experimental precipitation rate of iron carbonate under supersaturations of 7 to 150 at a temperature of 80°C.

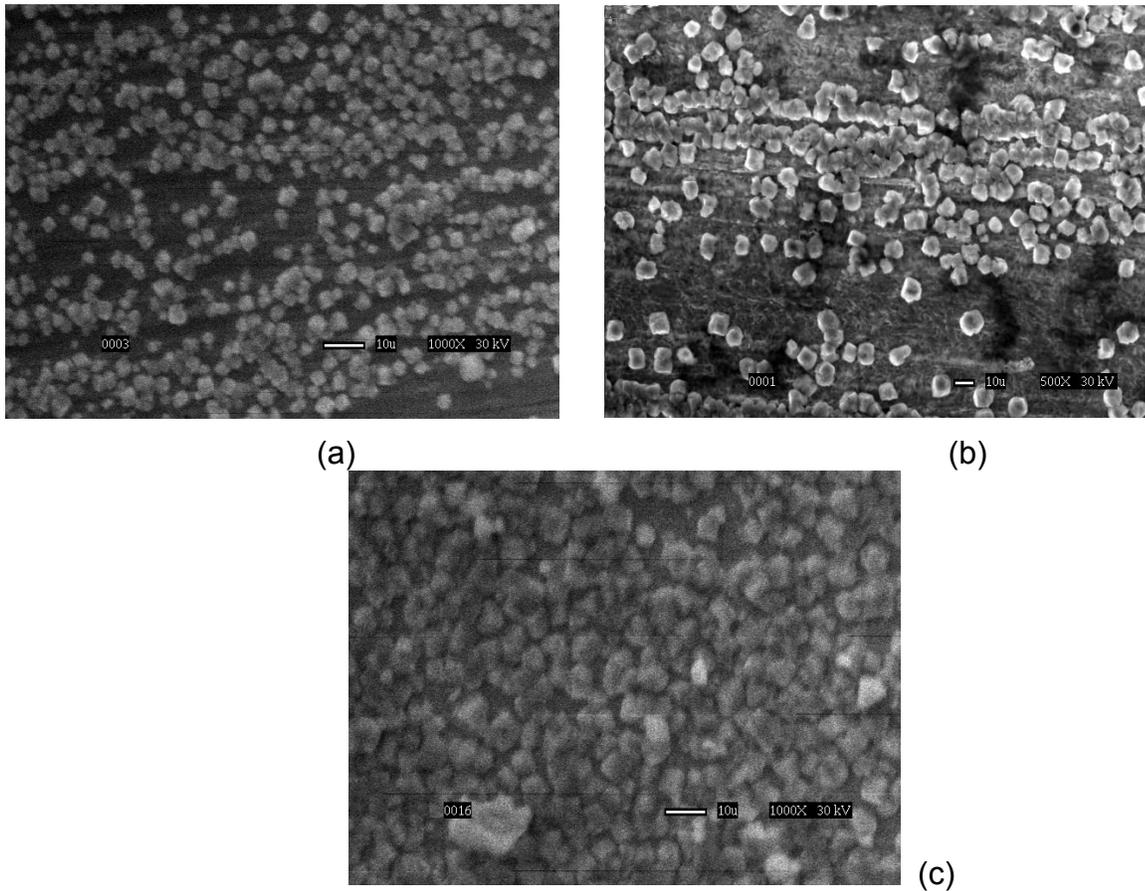


**Figure 3. Calculated precipitation rate of iron carbonate under supersaturations of 7 to 150 at a temperature of 80°C.**

Scanning electron microscopy (Figure 4) shows that there was almost no growth of iron carbonate scale when formed on the stainless steel or the inhibited carbon steel under similar conditions e.g. at a supersaturation of 30 after three days. The reason is that iron carbonate scale formed on the uninhibited carbon steel because corrosion leads to a much higher supersaturation at the steel surface than in the bulk solution. When the supersaturation increased to 150, more iron carbonate crystals precipitated on carbon steel than on stainless steel and inhibited carbon steel, as shown in Figure 5. In that case the scale precipitated on stainless steel and on the inhibited carbon steel was approximately 50% of that compared to corroding mild steel.



**Figure 4. Comparison of top views for specimens of the three different substrates, a) stainless steel, b) inhibited carbon steel, c) carbon steel under the conditions of pH 6.60, Fe<sup>2+</sup> = 10ppm, SS = 30, T = 80°C, stagnant conditions.**



**Figure 5. Comparison of the top views for specimens of the three different substrates, a) stainless steel, b) inhibited carbon steel, c) carbon steel under the conditions of pH 6.60,  $Fe^{2+}$  = 50ppm, SS = 150, T = 80°C, stagnant conditions.**

The experimental results were compared to predictions using MULTICORP V3.0, the multiphase flow and corrosion prediction model developed by Ohio University. The model was run for 15 hours under the conditions of pH 6.60,  $Fe^{2+}$  concentration of 50ppm, SS = 150, T = 80°C. One simulation was run each with inhibitor (assuming 99% efficiency) and without inhibitor. It was observed that in the presence of the inhibitor the  $Fe^{2+}$  concentration (Figure 6) as well as the pH (Figure 7) near the surface of the metal is lower than that in the absence of the inhibitor. This would lead to a lower supersaturation and a slower precipitation rate near the metal surface when the inhibitor is added. From the comparison of the scales obtained using the model (Figure 8), it was found that the thickness of the iron carbonate scale formed in the presence of the inhibitor was about 25% of the scale thickness formed in the absence of the inhibitor.

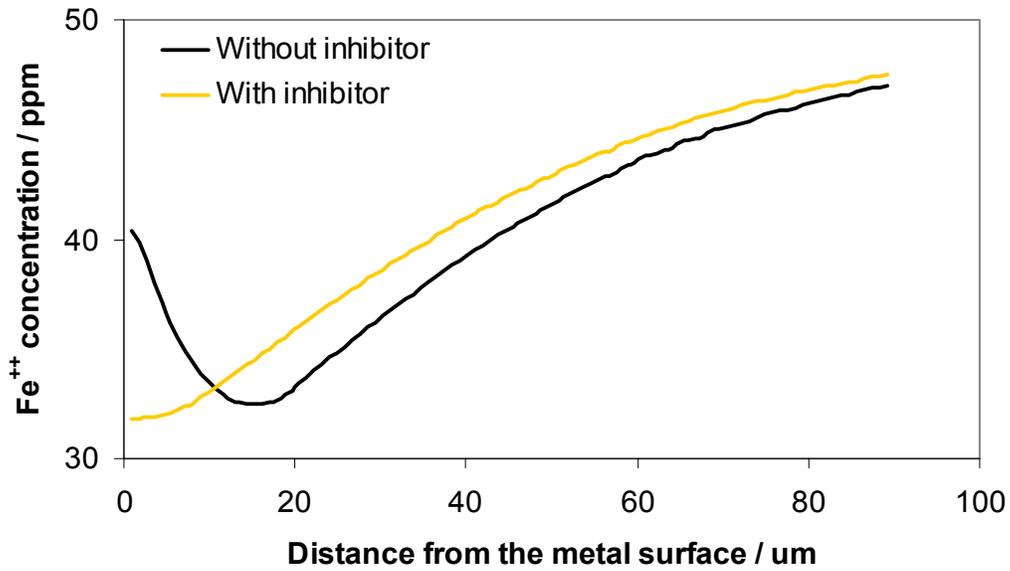


Figure 6. Fe<sup>2+</sup> concentration profile with and without the inhibitor obtained using MULTICORP V3.0 at pH 6.60, Fe<sup>2+</sup> = 50 ppm, SS = 150, T = 80°C.

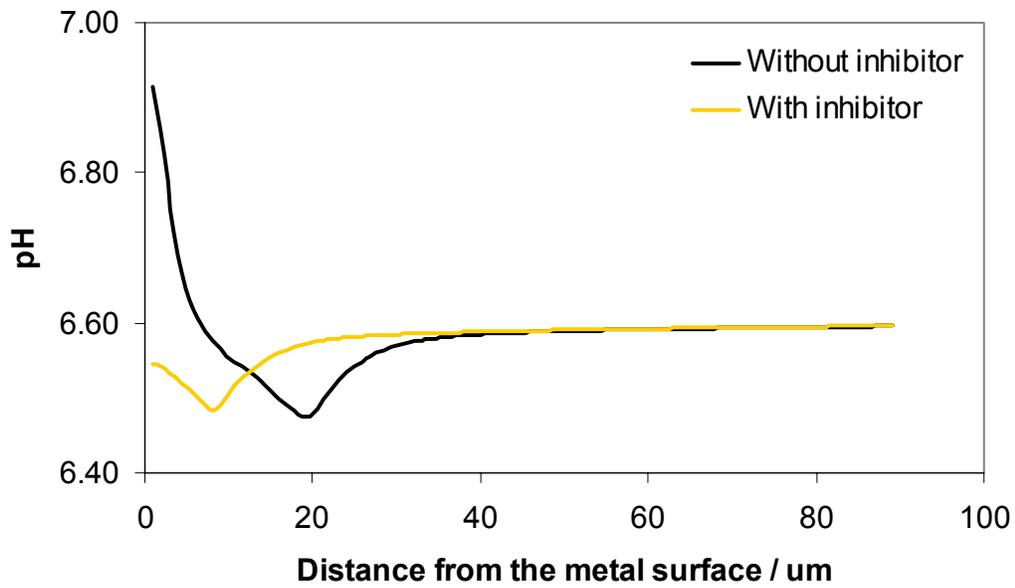
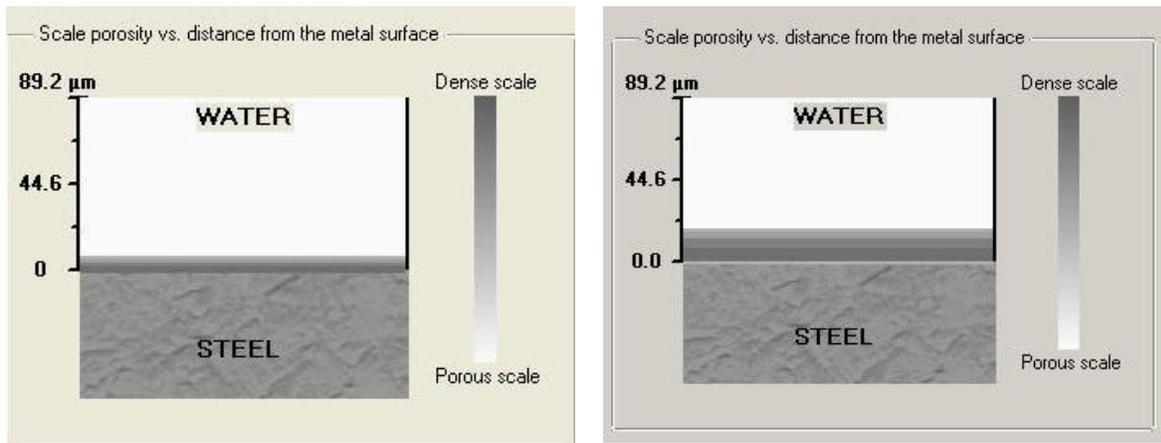


Figure 7. pH profile with and without the inhibitor obtained using MULTICORP V3.0 at pH 6.60, Fe<sup>2+</sup> = 50 ppm, SS = 150, T = 80°C.

(a)

(b)



**Figure 8. Comparison of the iron carbonate scale obtained (a) with and (b) without inhibitor using MULTICORP V3.0 at pH 6.60,  $Fe^{2+} = 50$  ppm,  $T = 80^{\circ}C$ .**

The model reinforces the experimental observations and helps explain them. In each case, as soon as the metal surface is exposed to the solution, iron carbonate begins to precipitate on it. Formation of iron carbonate leads to a drop in the concentration of iron and carbonate ions at the metal surface. The corrosion occurring under the porous iron carbonate scale and the diffusion of  $Fe^{2+}$  from the bulk solution replenishes the  $Fe^{2+}$  "lost" at the metal surface. In the presence of the inhibitors, the corrosion rate of the metal decreases, and the diffusion of  $Fe^{2+}$  from the bulk solution remains the only source of ions for precipitation at the metal surface. Since the precipitation of the iron carbonate is much faster than the rate of transportation of  $Fe^{2+}$  from the bulk of the solution to the surface, the precipitation becomes diffusion-controlled. This leads to slightly more acidic conditions at the metal surface, and, consequently, both the supersaturation level and the precipitation of iron carbonate decrease. Hence, in the absence of corroding conditions at the metal surface, there is little or no scale formed at the surface.

## Conclusions

The primary findings of this work are:

- The weight gain/loss (WGL) method is a reliable method to obtain the precipitation rate. The traditional iron concentration method used previously overestimates the precipitation rate.
- The precipitation rate of iron carbonate on carbon steel was higher than the one obtained on inhibited carbon steel or on stainless steel. It was found that corrosion beneath the scale was the major factor in scale formation on the uninhibited carbon steel.

## Literature Cited

Johnson, M. L., & Tomson, M. B. (1991). Ferrous carbonate precipitation kinetics and its impact CO<sub>2</sub> corrosion. *Corrosion/91*, Paper No. 268, NACE International, Houston, Texas.

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