# Influence of Acetic Acid on the Integrity and Protectiveness by an Iron Carbonate (FeCO<sub>3</sub>) Corrosion Product Layer

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The effect of undissociated acetic acid on the integrity of an iron carbonate (FeCO<sub>3</sub>) layer formed on platinum and X65 steel substrates is investigated. Experiments were conducted using buffered solutions with 0.8 mM to 5 mM undissociated acetic acid. For the platinum substrates, changes in the FeCO<sub>3</sub> layer were monitored via in situ electrochemical quartz crystal microbalance (EQCM) measurements. This investigation was supported by performing electrochemical experiments, under comparable conditions, on the X65 steel specimens, linking the integrity of FeCO<sub>3</sub> layer to its corrosion protection effect. The EQCM measurements revealed that the addition of acetic acid, at all concentrations tested here, caused partial dissolution of the FeCO<sub>3</sub> layer. The dissolution occurred selectively, with the outer layer dissolving first, leaving behind an inner FeCO<sub>3</sub> layer at the end of the immersion experiment. The electrochemical results revealed that introducing the acetic acid caused a sudden increase in the corrosion rate, which over time returned to a lower value similar in magnitude to that seen before addition of the acetic acid. This was attributed to the protection provided by the inner FeCO<sub>3</sub> layer, which was only mildly affected by the addition of acetic acid and was able to repair over time. It was proven that the dissolution of the protective FeCO<sub>3</sub> layer in the presence of acetic acid was not due to a small pH change but rather due to the formation of ferrous acetate complexes and changes in ionic strength, which decreases the FeCO<sub>3</sub> saturation values.

KEY WORDS: acetic acid, CO2 corrosion, ionic complexation, iron carbonate, mild steel

#### **INTRODUCTION**

**C** orrosion affected by the presence of organic acids especially acetic acid (CH<sub>3</sub>COOH or HAc) is a significant problem in the oil and gas industry.<sup>1-2</sup> In production and transportation, the internal surface of carbon steel lines can be exposed to an aqueous environment with dissolved acidic gases such as carbon dioxide (CO<sub>2</sub>) and hydrogen sulfide (H<sub>2</sub>S), which can lead to very high corrosion rates of the bare steel surface (order of 1 mm/y to 10 mm/y). In some conditions a protective iron carbonate (FeCO<sub>3</sub>) or iron sulfide (FeS) corrosion product layers can spontaneously form, thereby reducing the corrosion rate by one or more orders of magnitude. In such conditions, it has been suggested from field experience that the presence of HAc at concentrations higher than 0.1 mM to 1 mM, is a critical factor that can lead to failure of protective layers and high rates of localized corrosion.<sup>3-5</sup>

The effect of HAc dissolved in an aqueous environment on the kinetics of cathodic reactions has been extensively studied and is reasonably well understood.<sup>6-7</sup> It is now well established that the main role of the weak HAc is to increase the cathodic limiting current for hydrogen ion reduction, due to its ability to provide more hydrogen ions by dissociation. The longstanding hypothesis about direct reduction of undissociated HAc was recently shown to be incorrect, as it was proven that this reaction does not occur at measurable rates.<sup>6</sup> However, the effect of HAc on the anodic reaction is still controversial and not well understood. Some studies have reported HAc retarding the anodic reaction, others observed no significant change, and some have shown accelerated anodic kinetics.<sup>8-13</sup> The increased values of corrosion potential occurring with addition of the HAc have been attributed to the shifting balance between the enhanced cathodic kinetics and the depressed anodic kinetics.<sup>9,11</sup>

Studying the effect of HAc on the integrity and protectiveness of corrosion product layers, such as FeCO<sub>3</sub>, which forms in aqueous CO<sub>2</sub> corrosion, is of great practical importance, however, reliable studies are rare. In 1999 one of the first studies in this field was presented by Hedges and McVeigh,<sup>1</sup> who reported an increase of CO<sub>2</sub> corrosion rates of X65 mild steel in the presence of HAc. They speculated that this was due to the formation of the "thinner semiprotective FeCO<sub>3</sub> layer" in the presence of HAc, although no direct evidence of such a layer existing in their experiments was provided, making this appear more like a speculation than a conclusion. Given the pH range covered by Hedges and McVeigh's experiments (pH 4.0 to pH 5.8) and the operating temperature (60°C), it is likely that the solubility product of FeCO<sub>3</sub> was not exceeded in their experiments and even if it was the "semiprotective" FeCO<sub>3</sub> layers would not have formed easily at this temperature. This is corroborated by very high corrosion rates (in the range of 3 mm/y to 10 mm/y and even higher) being reported by the authors. It was also stated in the paper that the supposed thinning of the semiprotective FeCO<sub>3</sub> layer in the presence of acetate ions (Ac<sup>-</sup>) is because  $Ac^{-}$  can "solubilize the iron ions (Fe $^{2+}$ ) as they are formed, thus transporting them away from the steel surface."

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According to the authors this was because "iron acetate is more soluble than iron carbonate." The latter statement is correct; however, ferrous acetate is so soluble that it could not have formed as a solid given the experimental conditions being tested. Nevertheless, even if one can take issue with the interpretations of Hedges and McVeigh, they were on the right track when suggesting that the presence of Ac<sup>-</sup> can lead to dissolution of protective FeCO<sub>3</sub> layers, and have therefore inspired a number of follow-up studies by different authors.

One example is the study of Liu, et al.,<sup>14</sup> from 2008 who studied the effect of Ac<sup>-</sup> on N80 steel corrosion at 50°C. From their paper it is entirely unclear how they reached a similar conclusion as Hedges and McVeigh<sup>1</sup> given that formation of a protective FeCO<sub>3</sub> layer was not confirmed in their experiments conducted with or without Ac<sup>-</sup> present. This does not come as a surprise given the acidic pH range studied (pH 3.45 to pH 5.2), and the temperature (50°C) conditions where formation of FeCO<sub>3</sub> is not practically feasible. They presented one image of "an amorphous corrosion product layer" formed on the steel surface exposed in a CO<sub>2</sub> solution without Ac<sup>-</sup>, which was not there when Ac<sup>-</sup> was present and concluded that "when acetic acid or acetate was added the corrosion film became thin or vanished completely." Then based on a complex analysis of electrochemical impedance spectroscopy (EIS) measurements they arrived at a conclusion that "Ac<sup>-</sup> plays an important role in the anodic dissolution processes, which affect mainly the formation/adsorption of intermediates, and tends to form more soluble corrosion products." Given the limited amount of information presented in the paper of Liu, et al.,<sup>14</sup> it is difficult to evaluate or accept this argument.

Yet another study that somehow came up with a similar conclusion using different reasoning, was presented in 2009 by Zhang and Cheng.<sup>15</sup> The authors stated that "scale formed in the CO<sub>2</sub>-saturated formation water in the presence of HAc is less protective than that formed in the absence of HAc," with the scale being FeCO<sub>3</sub>. Their interpretation was that this happens because the "addition of HAc degrades the protectiveness of corrosion scale and thus enhances corrosion of steel by decreasing the FeCO<sub>3</sub> supersaturation in solution." They correctly state that the supersaturation decrease happens because HAc "acidifies the formation water," but then go onto say that "at a given pH and  $CO_2$  partial pressure, the  $HCO_3^-$  and  $CO_3^{2-}$ contents decrease in the presence of free HAc," which is not generally true. Furthermore, just like with the studies of Liu, et al.,<sup>14</sup> and Hedges and McVeigh<sup>1</sup> it is not clear how Zhang and Cheng<sup>15</sup> reach the conclusions about the effect of HAc on FeCO<sub>3</sub> when there is no proper evidence of FeCO<sub>3</sub> formation in any of their experiments. The SEM images they present do not show any clear evidence of FeCO<sub>3</sub> and given the reported experimental conditions (pH 5.18 and 60°C) it is not likely that protective FeCO<sub>3</sub> layers formed in any of their experiments.

In 2010 Nazari, et al.,<sup>16</sup> reported an investigation on the effect of HAc at different concentrations (0, 500 ppm, 1,000 ppm, and 2,000 ppm) on the formation of a FeCO<sub>3</sub> layer. Their results showed that increasing the concentration of HAc from 500 ppm to 2,000 ppm can impede the precipitation of FeCO<sub>3</sub> layer at 75°C. However, there was no attempt to control the pH in their experiments, hence the initial pH 6.5 measured without HAc decreased to pH 6.36 in the experiment at 500 ppm HAc, then to pH 6.04 at 1,000 ppm HAc, and finally to pH 4.72 at 2,000 ppm HAc. Any drift of the pH seen in 24 h long experiments conducted in 2.5 L glass cell, were not reported, neither was the concentration of ferrous ions in solution. Hence, it is difficult to assess the changes in FeCO<sub>3</sub> saturation levels in solution from

one experiment to another in order to compare them and deduce any effect on FeCO<sub>3</sub> layer formation. Yet one can say with sufficient confidence that the main effect of HAc on the formation of FeCO<sub>3</sub> layer in the experiments of Nazari and Allahkaram<sup>16</sup> was due to the decrease in pH with increasing HAc concentrations, from one experiment to another. While this behavior is reasonable and expected, it is not specific to HAc. Any other acid (weak or strong) that caused a decrease of solution pH would have had the same or similar effect on the integrity of the precipitated FeCO<sub>3</sub> layer.

Zhu, et al.,<sup>17</sup> presented a study in 2011 on the effect of HAc concentration (0, 1,000 ppm, 3,000 ppm, and 5,000 ppm) on the corrosion of N80 carbon steel. The high-pressure autoclave experiments conducted at partial pressure of carbon dioxide (pCO<sub>2</sub>) of 40 bar, at 90°C, lasted 120 h. The authors reported high time-averaged corrosion rates obtained by weight loss, varying between 0.5 mm/y and 5 mm/y, which increased linearly with HAc concentration. The FeCO<sub>3</sub> layer was detected on the steel surface in all conditions tested, with and without HAc. This can be explained by the amount of time the specimens were exposed to very aggressive conditions in the autoclave, where high corrosion rates led to a significant buildup of Fe<sup>2+</sup> in solution, accompanied by an increase in pH (neither were reported). This would have eventually led to the FeCO<sub>3</sub> solubility being exceeded in solution and formation of corrosion product layer on the steel surface. The authors reported increased pitting at higher HAc concentrations, although this was not corroborated by the SEM images presented in the paper, where a general roughening of the corroded steel surface is seen at higher HAc concentrations. The authors implied that this happened because: "the addition of HAc degraded the protectiveness of corrosion scale," even if they presented no evidence of the latter. Just like Zhang and Cheng<sup>15</sup> they attempt to explain this behavior by a decrease in FeCO<sub>3</sub> supersaturation as "at a given pH and CO<sub>2</sub> partial pressure, the concentrations of  $HCO_3^-$  and  $CO_3^{2-}$  decrease in the presence of free HAc," which is not correct for the case of ideal solutions.

Clarity on this subject matter was provided in an excellent but rarely referenced/acknowledged NACE conference paper by Gulbrandsen<sup>18</sup> from 2007. In long-term experiments, conducted at 80°C, where all of the critical parameters were properly measured and successfully controlled (pH, Fe<sup>2+</sup> concentration, HAc concentration, etc.), Gulbrandsen unraveled the relationship between FeCO<sub>3</sub> supersaturation and HAc concentration and their influence on formation of protective layers. He has clearly shown that the presence of HAc does not always lead to failure of FeCO<sub>3</sub> layers, as claimed in many of the abovementioned studies, without proper evidence or a correct explanation. It was shown that at high FeCO<sub>3</sub> supersaturations in solution (above 20 to 30), protective FeCO<sub>3</sub> layers formed, regardless of the presence of HAc. This was consistent with the results of Nafday and Nešić<sup>19</sup> who have also seen that at lower concentrations (up to 180 ppm undissociated HAc and FeCO<sub>3</sub> supersaturation of 32 and 162) HAc did not affect the protection provided by the FeCO<sub>3</sub> layer and the final corrosion rate. At lower FeCO<sub>3</sub> supersaturation (<20), when the driving force for formation and repair of FeCO<sub>3</sub> protective layers was smaller, Gulbrandsen has shown that HAc did have a negative impact on the protectiveness of the FeCO<sub>3</sub> layer. The effect was explained by the formation of a soluble ferrous acetate (FeAc<sup>+</sup>) complex in solution, which binds the ferrous ions and decreases the level of FeCO<sub>3</sub> supersaturation. The feasibility of this proposal was described in their NACE conference paper published the year before.<sup>20</sup> The effect of decreased supersaturation on the

# **SCIENCE** SECTION

corrosion rate was explained by using the concept of scaling tendency. In a series of subsequent papers, Gulbrandsen and his coauthors presented pit propagation studies in the presence of HAc. It has been shown there that the HAc concentration gradient between an artificial pit and the outer surface is the reason for the pit growth, up to a particular depth, after which the pit is depleted from HAc and the subsequent ohmic drop decreases the current.<sup>21-23</sup> Regrettably, many of the studies that followed did not build on the work of Gulbrandsen and his coauthors, something that will be corrected in the present paper.

The current paper presents a systematic study attempting to clarify when and how the presence of undissociated HAc can compromise the integrity of FeCO<sub>3</sub> layer and its corrosion protectiveness. In situ weight gain/loss measurements were made using the electrochemical quartz crystal microbalance (EQCM). In addition, electrochemical experiments were performed on the X65 (UNS K03014<sup>(1)</sup>) steel specimens under comparable experimental conditions to those of the EQCM, in order to relate the changes in FeCO<sub>3</sub> layer to the corrosion rate.

#### **EXPERIMENTAL PROCEDURES**

#### 2.1 | The Electrochemical Quartz Crystal Microbalance Measurements

EQCM measurements were selected as an in situ mass change detection method to investigate the effect of HAc on the integrity of FeCO<sub>3</sub> layer. The experiments were performed in a glass cell. A typical three-electrode electrochemical setup was used, including a platinum-coated quartz crystal as the working electrode (WE), a platinum wire as the counter electrode (CE), and an external saturated silver/silver chloride (Ag/AgCI [KCl<sub>sat</sub>]) reference electrode (RE) connected to the cell via a Luggin capillary. The pH of the bulk solution was measured using an immersed glass pH electrode. The temperature of the electrolyte was measured using a thermocouple immersed in the solution linked to a controller and a hot plate. The experimental temperature was maintained within ±1°C in all experiments. A reflux condenser was used to minimize the loss of solution. A detailed schematic representation of the glass cell is shown in Figure 1.

For each experiment, the glass cell was filled with 2 L of 0.1 wt% NaCl solution (prepared with deionized [DI] water). Before each experiment, CO<sub>2</sub> was continuously bubbled through the electrolyte for approximately 1 h. The CO<sub>2</sub> bubbling was continued during the entire experiment. This was done in order to ensure that all of the dissolved oxygen was removed, and the solution was saturated with CO<sub>2</sub>. An Orbisphere 410<sup>T</sup> oxygen meter and sensor capable of measurements down to 0.1 ppb [O<sub>2</sub>] was used to ensure the glass cell was sealed properly and that oxygen was purged from the aqueous solution prior to experimentation starting. With initially high purge rates of CO<sub>2</sub>, the oxygen concentration decreased below 40 ppb [O2] within 5 min, with additional purging required up to 1 h to get below 1 ppb [O2]. As needed, a deoxygenated aqueous solution of hydrochloric acid (HCI) or sodium bicarbonate (NaHCO<sub>3</sub>) was added to the cell to adjust the pH.

The platinum-coated quartz crystal WE was used; being a noble metal, the platinum does not corrode, making it possible to



FIGURE 1. Schematic representation of the glass cell setup used for the EQCM measurements.

measure the mass gain and loss of the FeCO<sub>3</sub> laver without any interference by the corrosion of the underlying substrate. This was not the case with the obvious alternative-the iron-coated quartz crystal. The thickness of the vapor-deposited iron layer on the quartz crystal is typically around 1 µm and would therefore corrode away before the precipitation process was complete; the layer of iron is also too smooth and would inhibit the nucleation of FeCO<sub>3</sub>. Therefore, the iron-coated quartz crystal, although available, was found not to be suitable for this purpose (after many failed attempts). During the experiments, the platinumcoated guartz crystal WE was cathodically polarized to -700 mV<sub>Aq/AqCl(KClsat</sub>) in order to mimic the corrosion potential of mild steel corroding in a CO<sub>2</sub> aqueous solution. Although it is acknowledged that the precipitation of FeCO<sub>3</sub> on the platinum substrate is different than that happening on mild steel, the polarization was used to try and create similar water chemistry conditions at the metal surface and facilitate the precipitation of FeCO<sub>3</sub>.

ments	
Experimental Variable	Content
Electrolyte	0.1 wt% NaCl
WE material	Platinum-coated quartz crystal
Temperature	80°C
CO <sub>2</sub> partial pressure	0.53 bar
Undissociated HAc	0 mM, 1 mM, 3 mM, and 5 mM (0, 60 ppm, 180 ppm, and 300 ppm)
Initial pH	6
Initial $S_{FeCO_3}$	200
Flow	Stagnant

Table 1. Experimental Conditions for the EQCM Measure-

<sup>&</sup>lt;sup>(1)</sup> UNS numbers are listed in *Metals & Alloys in the Unified Numbering System*, published by the Society of Automotive Engineers (SAE International) and cosponsored by ASTM International.

<sup>&</sup>lt;sup>†</sup> Trade name.

The detailed experimental conditions for the EQCM measurements are provided in Table 1. For this set of experiments, the initially high FeCO3 saturation value (SFeCO3) was achieved by the addition of ferrous chloride (FeCl<sub>2</sub>) solution. The FeCl<sub>2</sub> solution was made from deoxygenated DI water and crystalline Fisher Scientific certified iron (II) chloride tetrahydrate, so that each mL injected would add the desired amount of Fe<sup>2+</sup> ions into the glass cell. Aqueous solutions of glacial HAc at three different undissociated HAc concentrations (1 mM, 3 mM, and 5 mM) were selected to study their effect on solubility of the FeCO<sub>3</sub> layer. The HAc was injected into the system by the means of an automated syringe pump as a deoxygenated buffered solution to avoid a simultaneous change in pH with the addition of HAc. When the gain in mass measured by the EQCM plateaued and saturation leveled at  $S_{FeCO_3} \approx 10$ , the buffered HAc solution was added, after adjusting the pH to be as close as possible to the measured solution pH in the glass cell at the time of injection (which was different from the initial pH of the solution).

### 2.2 | Electrochemical Measurements Using an X65 Steel Electrode

In order to investigate the effect of undissociated HAc on the corrosion protection offered by a precipitated FeCO<sub>3</sub> layer, comparable experiments to those performed by using EQCM were performed on X65 mild steel specimens, using the rotating cylinder electrode (RCE) configuration. The electrochemical experiments were performed in a glass cell similar to the one previously shown in Figure 1. A three-electrode setup, including the X65 RCE as the WE (with the exposed area of 1.78 cm<sup>2</sup>), a platinum wire as the CE, and a saturated Ag/AgCI (KCI<sub>sat</sub>) RE, was used. Before the experiment, the mild steel WE was wet ground using silicon carbide abrasive papers up to 600 grit followed by rinsing with DI water and isopropanol and drying with nitrogen, before being mounted onto the specimen holder and inserted into the solution shortly after. The composition of X65 mild steel in wt% was as follows: C 0.14%, Si 0.25%, Mn 1.18%, P 0.012%, S 0.003%, Al 0.033%, Cr 0.15%, Mo 0.16%, Nb 0.027%, and the balance Fe. The details of the experimental conditions are provided in Table 2.

The first set of experiments was focused on determining the influence of the HAc concentration on the  $FeCO_3$  layer at a constant pH. As compared to the prior EQCM measurements, this series of experiments used lower concentrations of undissociated HAc. The goal was to try and identify if the effect of

Measurements			
Experimental Variable	Content		
Electrolyte	3 wt% NaCl		
WE material	X65		
Temperature	80°C		
CO <sub>2</sub> partial pressure	0.53 bar		
Undissociated HAc	0.8 mM, 1.6 mM, and 3 <sup>(A)</sup> mM (48 ppm, 96 ppm, and 180 ppm)		
Initial pH	6.3		
Initial S <sub>FeCO3</sub>	100 and 200 <sup>(A)</sup>		
Rotation velocity	Stagnant and 1,000 rpm		
<sup>(A)</sup> Only for surface characterization.			

HAc extends beyond its ability to acidify the solution. Therefore, HAc was added into the system as a buffered solution at the same pH as the main solution at that time. The acetate ion (CH<sub>3</sub>COO<sup>-</sup>) used to make up the buffered solution was provided by dissolving a soluble salt (sodium acetate trihydrate [NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>·3H<sub>2</sub>O], certified, Fisher Scientific). The speciation of all of the solutions used in experiments (EQCM and electrochemical measurements) was calculated using a water chemistry model, reported elsewhere.<sup>24</sup> The effect of flow was investigated by using a RCE at 1,000 rpm. In this case, the initial pH of the solution was set at 6.3 and the concentration of undissociated HAc at 0.8 mM. Linear polarization resistance (LPR) measurements were conducted by polarizing the WE from -5 mV to 5 mV vs. the open-circuit potential (E<sub>ocp</sub>) at a scan rate of 0.1 mV/s. Values of E<sub>ocp</sub> were recorded throughout the experiments as well. The solution resistance was measured independently using EIS measurements. The EIS was done by applying an oscillating potential (5 mV rms) at the  $E_{ocp}$  to the WE in the frequency range between 100 kHz and 1 mHz.

Using the data acquired from the LPR experiments, the corrosion rate was calculated as follows:<sup>25</sup>

$$i_{corr} = \frac{\beta_a \cdot \beta_c}{2.3R_p \cdot (\beta_a + \beta_c)} = \frac{B}{R_p}$$
(1)

$$CR = 3.27 \times 10^{-3} \frac{EW \cdot i_{corr}}{\rho}$$
 (2)

In Equation (1),  $i_{corr}$  is the corrosion current density ( $\mu A/cm^2$ ),  $\beta_a$  and  $\beta_c$  are the anodic and cathodic Tafel slopes,  $R_p$  is the measured polarization resistance ( $\Omega \cdot cm^2$ ). The  $\beta_a$  and  $\beta_c$  were set at 40 mV/dec and 120 mV/dec, respectively, giving the B value of 13 mV.  $R_p$  was determined by the slope of the current voltage curve ( $\partial E/\partial i$ ) at  $E_{ocp}$ . In Equation (2), EW is the equivalent weight (g),  $\rho$  is density (g/cm<sup>3</sup>), and 3.27  $\times 10^{-3}$  is the conversion constant to mm/y.

## 2.3 | FeCO<sub>3</sub> Layer Characterization

After the EQCM and electrochemical experiments, ex situ analyses of the morphology and compositions of the corrosion product layers were conducted by using various analytical techniques. The surface morphologies and composition of the precipitated layer was examined using scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDS), and Raman spectroscopy. Cross-sectional analysis was performed by using transmission electron microscopy (TEM) with focused ion beam (FIB) milling.

## RESULTS

## 3.1 | Effect of HAc on FeCO<sub>3</sub> Layer Formed on Platinum

The EQCM measurement was used as an in situ technique to evaluate the dissolution of FeCO<sub>3</sub> due to the presence of HAc at various concentrations (1 mM, 3 mM, and 5 mM of undissociated HAc). As mentioned above, these experiments were performed at the temperature of 80°C, CO<sub>2</sub> partial pressure of 0.53 bar, an initial pH of 6.0, and the initial S<sub>FeCO<sub>3</sub></sub> of 200. The results are shown in Figure 2. Following the immersion in a highly supersaturated solution, the EQCM registered a mass increase as a result of FeCO<sub>3</sub> precipitation on the surface of platinum:

$$Fe^{2+} + CO_3^{2-} \leftrightarrows FeCO_3 \tag{3}$$

with the net reaction being from left to right, due to the saturation value  $S_{FeCO_3}\gg$  1 (also called supersaturation).



**FIGURE 2.** Mass change vs the immersion time for the cathodically polarized ( $-700 \text{ mV}_{Ag/AgCl[KClsat]}$ ) platinum-coated quartz crystal electrode exposed to a 0.1 wt% NaCl solution at initial pH 6.0, 80°C, and 0.53 bar pCO<sub>2</sub>, initial S<sub>FeCO3</sub> = 200 before and after injection of a buffered solution containing different amounts of undissociated HAc: (a) no addition of HAc, (b) 1 mM of undissociated HAc, (c) 3 mM of undissociated HAc, and (d) 5 mM of undissociated HAc.

Supersaturation is the driving force for the precipitation process and it is here defined as the extent of departure from equilibrium for Reaction (3) as defined by the solubility product  $(K_{sp} = (c_{Fe^{2+}})_{eq} \cdot (c_{CO_{s}^{2-}})_{eq})$ , and quantified as follows:

$$S_{FeCO_3} = \frac{C_{Fe^{2+}} \cdot C_{CO_3^{2-}}}{K_{so}}$$
 (4)

The ferrous, Fe<sup>2+</sup>, ion concentration  $c_{Fe^{2+}}$  was directly measured, while the carbonate,  $CO_3^{2-}$ , ion concentration  $c_{CO_3^{2-}}$  was calculated from the measured pH, knowing the CO<sub>2</sub> partial pressure, pCO<sub>2</sub>. The solubility product of FeCO<sub>3</sub> is a function of temperature and ionic strength:<sup>26</sup>

$$K_{sp} = 10^{-59.3498 - 0.041377 \times T_{K} - \frac{2.1963}{T_{K}} + 24.5724 \times \log(T_{K}) + 2.518 \times I^{0.5} - 0.657 \times I}$$
(5)

where  $T_{\rm K}$  is the temperature (K) and I is the ionic strength of the solution. As the majority of dissolved  ${\rm Fe}^{2^+}$  ions were consumed by precipitation within the first 24 h, the net

precipitation rate slowed down and eventually approached zero, as  $S_{FeCO_3}$  decreased from the initial 200 to below 10, thereby reducing the driving force for precipitation. During this time, the pH of the solution also decreased from pH 6 to pH 5.4, due to the consumption of the  $CO_3^{2^-}$  ions by FeCO<sub>3</sub> precipitation, which caused the dissociation reactions of the weak acids (bicarbonate ion and carbonic acid):

$$\mathsf{HCO}_3^- \leftrightarrows \mathsf{H}^+ + \mathsf{CO}_3^{2^-} \tag{6}$$

$$H_2CO_3 \leftrightarrows H^+ + HCO_3^- \tag{7}$$

to move from the left to right, thereby preserving equilibrium. When the buffered HAc solution (at the same pH as the main solution) was injected into the system, a decrease in mass was observed indicating partial dissolution of the FeCO<sub>3</sub> layer. The measured decrease in the mass was proportional to the concentration of HAc: 11% of the FeCO<sub>3</sub> layer was lost at 1 mM HAc, 46% of the FeCO<sub>3</sub> layer dissolved at 3 mM HAc, and

44% of the FeCO<sub>3</sub> layer dissolved at 5 mM HAc. The details of the change in mass, pH, and  $S_{\rm FeCO_3}$  values, as shown on the curves in Figure 2, are provided in Table 3. Apparently, the addition of the buffered HAc with the same pH as the original solution led to a partial dissolution of FeCO<sub>3</sub> layer,

<b>Table 3.</b> Experimental Results During the EQCM Measurement of $FeCO_3$ Dissolution in the Presence of Various Undissociated HAc Concentrations <sup>(A)</sup>					
Stage	Δm (µg/cm²)	рН	S <sub>FeCO₃</sub>		
1 mM undissociated HAc					
I	989	5.41	13		
П	955	5.29	9.16		
3 mM undissociated HAc					
Ι	1,639	5.37	11.1		
П	866	5.20	4.6		
5 mM undissociated HAc					
I	1,797	5.40	10.5		
II	994	5.13	3.6		
<sup>(A)</sup> Stages I and II are before and after adding HAc, respectively.					

accompanied by a decrease in both the pH and  $S_{FeCO_3}$  values. This will be discussed later in the manuscript.

The SEM images of the specimens collected at the end of the experiments are presented in Figure 3. For the specimen after the "blank" test (conducted in the absence of HAc), the surface is fully covered by FeCO<sub>3</sub> (as confirmed below), showing a plate-like morphology with the occasional presence of prismatic crystals (Figure 3[a]). The present study did not focus on the factors that affect the precipitation of an FeCO<sub>3</sub> layer, normally happening on the surface of iron or steel, as this was done and presented in an earlier publication.<sup>27</sup> There, the pH was shown to change the morphology of FeCO<sub>3</sub> from prismatic crystals obtained at pH 6.6 to plate-like crystals formed at pH 6.0. Using various characterization techniques, including XPS and Raman spectroscopy, it was proven that regardless of the different morphologies, the composition was FeCO<sub>3</sub> in all cases.

Following addition of HAc (at different concentrations), the appearance of the surface layer has completely changed (Figures 3[b], [c], and [d]). The FeCO<sub>3</sub> plates have disappeared (dissolved), and the surface remained partially covered by FeCO<sub>3</sub> prismatic crystals, with some "bare" prism-free areas observed between the visible crystals. The specimens from the blank and the experiment with 3 mM HAc were selected here for further surface characterization. The results of Raman spectroscopy done on these specimens are depicted in Figure 4. The two main characteristic peaks of FeCO<sub>3</sub> (siderite)





**FIGURE 3.** SEM image of the platinum-coated quartz crystal electrode surface covered with FeCO<sub>3</sub> crystals exposed to a 0.1 wt% NaCl solution at initial pH 6.0, 80°C, and 0.53 bar pCO<sub>2</sub>, supersaturated with FeCO<sub>3</sub> (initial  $S_{FeCO_3} = 200$ ) following injection of a buffered solution containing different amounts of undissociated HAc: (a) no addition of HAc, (b) 1 mM of undissociated HAc, (c) 3 mM of undissociated HAc, and (d) 5 mM of undissociated HAc.



**FIGURE 4.** SEM image of the platinum-coated quartz crystal electrode surface covered with  $FeCO_3$  crystals exposed to a 0.1 wt% NaCl solution at initial pH 6.0, 80°C, and 0.53 bar pCO<sub>2</sub>, supersaturated with  $FeCO_3$  (initial  $S_{FeCO_3} = 200$ ) following injection of a buffered solution containing different amounts of undissociated HAc: (a) no addition of HAc, and (b) 3 mM undissociated HAc. (c) Results of Raman spectroscopy of the surface of specimens shown in (a) and (b).

at 292 cm<sup>-1</sup> and 1,087 cm<sup>-1</sup> wave numbers are detected for both specimens.<sup>28</sup> According to the results of Raman spectroscopy analysis of siderite and chukanovite presented in the paper by Michelin, et al.,<sup>29</sup> the minor peaks at 655 cm<sup>-1</sup>, 726 cm<sup>-1</sup>, and 500 cm<sup>-1</sup> might be attributed to either FeCO<sub>3</sub> or Fe<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub> (chukanovite) or both. Unfortunately, as the peaks for these two phases are too close, it is not possible to distinguish between them using Raman spectroscopy technique. It is not clear which of these phases or any other phases are related to the peaks at 1,309 cm<sup>-1</sup> and 1,711 cm<sup>-1</sup> that are

observed in the spectrum of the specimen before exposure to HAc (the green line in Figure 5[c]). However, the results of alternative characterization analysis (XPS) support the idea that the main phase in the corrosion product layer was FeCO<sub>3</sub>.<sup>27</sup>

The measurements on the specimen from the experiment with 3 mM HAc were performed both in the area covered by  $FeCO_3$  prismatic crystals and in the "bare" areas between the prisms. Interestingly, both areas show the presence of  $FeCO_3$ , meaning that the "bare" areas between the prisms were not depicting the bare platinum surface but were actually covered by



**FIGURE 5.** (a) SEM image of the cross-sectional view of the platinum-coated quartz crystal electrode surface covered with  $FeCO_3$  crystals exposed to a 0.1 wt% NaCl solution at initial pH 6.0, 80°C, and 0.53 bar pCO<sub>2</sub>, supersaturated with  $FeCO_3$  (initial  $S_{FeCO_3}$  = 200) following injection of a buffered solution containing 3 mM undissociated HAc, and (b) electron diffraction pattern of a prismatic crystal.

a thin FeCO<sub>3</sub> layer, which was not distinguishable in the SEM images. Considering the results of Raman spectroscopy, no meaningful difference was observed between the two specimens (blank and 3 mM HAc) in terms of the composition of the layer present on the surface.

Figure 5 presents the SEM image of the cross-sectional view of the specimen exposed to 3 mM HAc. As expected from the SEM images (Figure 3[c]), the remaining  $FeCO_3$  prismatic crystals are recognizable. It can also be seen that the "bare" area between the prisms is also covered by a layer, which is thin and adherent to the metal surface, just as the Raman spectroscopy results suggested. The electron diffraction pattern of the prismatic crystals confirms that they are indeed  $FeCO_3$ .

Now that it is established that some  $FeCO_3$  crystals that formed by precipitation were dissolved due to HAc injection, let us try to answer why this happened. As noted above, the buffered HAc solution was injected at the same pH as the main solution supersaturated with FeCO<sub>3</sub>; however, this led to a small decrease in the pH of the main solution by 0.1 to 0.3 units, as shown in Table 3. One can wonder if this small pH decrease (acidification) was the main reason that led to the partial dissolution of the FeCO<sub>3</sub> layer, as has been suggested by other researchers.<sup>15,17</sup> To answer this question, an extra set of EQCM experiments was performed for which the same kind of scenario was created: formation of FeCO<sub>3</sub> layer followed by the same small drop in pH, but this time achieved by injecting a deoxygenated solution of strong HCl acid (rather than weak HAc). The results are provided in Figure 6.

As seen in Figure 6, the small change in pH caused a very small mass decrease, as detected by the EQCM. For the case when the injection of the HCl solution led to a pH drop of 0.2 units, the change in mass of the FeCO<sub>3</sub> was 20  $\mu$ g/cm<sup>2</sup>, which is significantly lower than what was measured when the buffered HAc solution was injected and caused a similar decrease in pH (0.2 units), when the mass change of FeCO<sub>3</sub> was orders of magnitude higher: 773 µg/cm<sup>2</sup>. The similar outcome was seen when the injection of HCl caused a pH drop by 0.35 units and the mass change in FeCO<sub>3</sub> was 155  $\mu$ g/cm<sup>2</sup>, which is much smaller than what was measured when buffered HAc solution was injected and caused a similar pH drop (0.3 units) when the mass change of FeCO<sub>3</sub> was much higher—803  $\mu$ g/cm<sup>2</sup>. This is corroborated by the SEM images and EDS analysis shown in Figures 7 and 8, which show negligible change in the morphology, FeCO<sub>3</sub> coverage, and chemical composition after the



**FIGURE 6.** Values of mass change vs. the immersion time for the cathodically polarized (–700  $mV_{Ag/AgCl[KCIsat]}$ ) platinum-coated quartz crystal electrode surface covered with FeCO<sub>3</sub> crystals exposed to a 0.1 wt% NaCl solution at initial pH 6.0, 80°C, and 0.53 bar pCO<sub>2</sub>, supersaturated with FeCO<sub>3</sub> (initial S<sub>FeCO<sub>3</sub></sub> = 200) following injection of a deoxygenated HCl solution, introducing (a) 0.2 and (b) 0.35 units pH drop.



**FIGURE 7.** (a) SEM images of the platinum-coated quartz crystal electrode surface covered with  $FeCO_3$  crystals exposed to a 0.1 wt% NaCl solution at initial pH 6.0, 80°C, and 0.53 bar pCO<sub>2</sub>, supersaturated with  $FeCO_3$  (initial  $S_{FeCO_3}$  = 200) and following injection of a deoxygenated HCl solution, introducing (b) 0.2 and (c) 0.35 units pH drop.

# SCIENCE SECTION



**FIGURE 8.** (a) The result of EDS analysis of the platinum-coated quartz crystal electrode surface covered with  $FeCO_3$  crystals exposed to a 0.1 wt% NaCl solution at initial pH 6.0, 80°C, and 0.53 bar pCO<sub>2</sub>, supersaturated with  $FeCO_3$  (initial  $S_{FeCO_3}$  = 200) and following injection of a deoxygenated HCl solution, introducing (b) 0.2 and (c) 0.35 units pH drop.

HCl solution injection, when compared to the surface prior to the injection (i.e., from the "blank" test). Therefore, it can be concluded that the small drop in pH caused by the injection of the buffered HAc solution was not the main cause for dissolution of the FeCO<sub>3</sub> layer, and one needs the look at other possible causes. One clue was given by Gulbrandsen:<sup>18</sup> the formation of iron acetate complexes in solution. The other could be related to the change of ionic strength of solution following the injection of HAc. Both possibilities will be explored in the *Discussion* section below. But for now, let us turn our attention to the effect of the injection of HAc on the actual corrosion rate of X65 mild steel protected by an FeCO<sub>3</sub> layer.

# 3.2 | Effect of HAc on the Protective FeCO<sub>3</sub> Layer Formed on X65 Steel and the Resulting Corrosion Rate

In order to link the observed results showing the effect of HAc on the integrity of the  $FeCO_3$  layer formed on the platinum substrate to that formed under similar conditions on X65 mild steel and to investigate the effect on the resulting corrosion rate, a set of electrochemical experiments was conducted as outlined above.

The X65 steel corrosion rate measurements are presented in Figure 9. The bare steel corrosion rates seen at the beginning of the experiments started out relatively high: approximately 1 mm/y. This value decreased to approximately



**FIGURE 9.** Variation of corrosion rate and  $E_{ocp}$  vs. the immersion time for the X65 steel specimen exposed to a 3 wt% NaCl solution at initial pH 6.3, 80°C, and 0.53 bar pCO<sub>2</sub>, supersaturated with FeCO<sub>3</sub> (initial  $S_{FeCO_3} = 100$ ) before and after injection of a buffered solution containing (a) 0.8 mM undissociated HAc, under stagnant condition, (b) 1.6 mM undissociated HAc, under stagnant condition, and (c) 0.8 mM undissociated HAc, under the rotation speed of 1,000 rpm.

0.3 mm/y or lower after another few days of immersion, due to the precipitation of a protective FeCO<sub>3</sub> layer (composition will be confirmed below). As the corrosion rates decreased, the values of the open-circuit potential ( $E_{ocp}$ ) initially decreased as well, indicating a diffusion barrier being formed. As the corrosion rate decreased further, the  $E_{ocp}$  shifted toward more positive values, which suggest pseudo-passivation of the surface by the precipitating FeCO<sub>3</sub> layer, as explained by Han, et al.<sup>30</sup> Following the addition of the buffered HAc solution, the corrosion rates increased, then reached a peak and decreased back to similar low levels as were seen before addition of HAc. This suggests that any damage/dissolution to

the protective  $FeCO_3$  layer due to HAc was repaired by further precipitation of  $FeCO_3$ .

When having the flow (RCE at 1,000 rpm), Figure 9(c) shows that the high corrosion rate that was caused by the addition of the buffered HAc solution remained high until the end of the experiment, i.e., the layer could not be repaired as happened in stagnant conditions. This is due to an increase in turbulent mixing and the higher rate of diffusion of species between the bulk and the steel surface.<sup>31-32</sup>

According to the SEM images showing the surface of the X65 mild steel collected at the end of the experiments, a significant loss of  $FeCO_3$  prismatic crystals following the addition of HAc is observed (Figures 10[b] and [c]). The loss seemed to be more severe when the concentration of HAc was higher. These results are in agreement with those presented earlier for the platinum substrate (Figure 3). The observations confirm that the solubility of the  $FeCO_3$  increased with the addition of the buffered HAc, even if the pH change was minimal.

The combined effect of the flow and HAc removed even more of the FeCO<sub>3</sub> prismatic crystals (Figure 10[d]). In this case, the "bare" areas without any FeCO<sub>3</sub> prismatic crystals seemed more porous (compared to the one seen after exposure to stagnant condition (Figure 10[b]), supporting the electrochemical measurements in Figure 9(c), which indicated the nonprotective nature of the remaining FeCO<sub>3</sub> layer.

For further analytical characterization, one specimen was exposed in similar conditions as those listed in Figure 9(b) but this time an even more concentrated HAc solution (3 mM HAc at pH 6.3) was added. The results of EDS analysis of the surface show the presence of iron (Fe), oxygen (O), and carbon (C) when analyzing the remaining prismatic crystals, as well as the "bare" areas in between (Figures 11[b] and [c]). The EDS analysis of the "bare" areas between the prisms show lower intensity peaks of Fe, O, and C, the constituent elements that form FeCO<sub>3</sub>, compared to the EDS results of the prismatic crystals; however, this elemental analysis is not conclusive.

A more accurate examination of this specimen and the blank specimen was conducted by making cross-sectional FIB samples and by electron diffraction pattern analysis using a TEM. Figure 12 depicts these results. The Bragg reflections (interplanar spacing [ $d_{hkl}$ ]) obtained from the lattice planes for the prismatic crystals correspond to the diffraction patterns of FeCO<sub>3</sub>.

In all of the images shown above, it is very important to note the "two-layered" structure of the precipitated FeCO<sub>3</sub>, which has been previously reported.<sup>33-37</sup> The outer layer consisted of either prisms or plates, which sit on top of a denser inner layer (indicated in Figure 12[a]). It is believed that this much thinner inner layer, which is adherent to the steel substrate, is the one that holds the key to corrosion protection by blocking the active electrochemical sites, leading to pseudo-passivation, seen in Figure 9 above. The outer, more porous layer offers a diffusion barrier and is not as effective at reducing the corrosion rate, which is controlled by a slow chemical reaction (CO<sub>2</sub> hydration) and not diffusion. The outer layer which is a diffusion barrier forms first (as plates and prisms) shown in Figures 3(a) and 10(a) and its main role is to create favorable conditions at the steel surface (high pH and ferrous ion concentration) so that the much more protective inner FeCO<sub>3</sub> layer can form. This is often missed when looking at SEM images of mild steel surfaces exposed to CO<sub>2</sub> solutions, when all of the attention is on the appearance and properties of the outer FeCO<sub>3</sub> layer. The recent studies by Ingham, et al.,<sup>38</sup> from



(c)

(d)

**FIGURE 10.** SEM image of the X65 steel specimen exposed to a 3 wt% NaCl solution at initial pH 6.3, 80°C, and 0.53 bar pCO<sub>2</sub>, supersaturated with FeCO<sub>3</sub> (initial  $S_{FeCO_3}$  = 100) following injection of a buffered solution containing different amounts of undissociated HAc: (a) no addition of HAc, (b) 0.8 mM undissociated HAc, under stagnant condition, (c) 1.6 mM undissociated HAc, under stagnant condition, and (d) 0.8 mM undissociated HAc, under rotation speed of 1,000 rpm.

2015 and Hassan Sk, et al.,<sup>32</sup> from 2017 which present an unprecedented view into the kinetics of the processes of FeCO<sub>3</sub> layer formation by using synchrotron small- and wide-angle x-ray scattering results, offer a clue as to how the two-layered FeCO<sub>3</sub> could have formed. In accordance with their findings, it can be postulated that the outer layer with prismatic crystals was formed by the classical dissolution-precipitation mechanism (iron dissolution followed by iron carbonate precipitation), as described above. Following Ingham, et al.,<sup>38</sup> and Hassan Sk, et al.,<sup>32</sup> it can now be postulated that the inner that the inner FeCO<sub>3</sub> layer could have been formed by the alternative "solid-state" oxidation reaction:

$$Fe + CO_3^{2-} \rightarrow FeCO_3 + 2e^-$$
 (8)

where solid iron FeCO<sub>3</sub> is formed directly by oxidizing iron from the steel in the presence of  $CO_3^{2^-}$ .

When the steel specimens were exposed to HAc, a lower number of  $FeCO_3$  prismatic crystals survived on the surface (confirmed by the electron diffraction pattern in Figure 12[d]). Nonetheless, the entire surface, even the "bare" areas between

the prisms, are covered by a layer which is proven to be  $FeCO_3$ . This can be seen in Figure 12(b) even when accounting for the considerable challenges of FIB sample preparation in this case.

#### DISCUSSION

Experimental results have demonstrated that an FeCO<sub>3</sub> layer, which was formed on both platinum and X65 steel, partially dissolved when exposed to HAc (Figures 3 and 10). The simplest explanation is that this happened due to a decrease in pH (increase in the concentration of H<sup>+</sup> ions, c<sub>H</sub>.). This is to be expected, because HAc is a weak acid, i.e., it is only partially dissociated, according to:

$$HAc \leftrightarrows H^+ + Ac^- \tag{9}$$

When a weak HAc solution is injected into a  $CO_2$ saturated aqueous solution (without any Ac<sup>-</sup> present), it leads to a decrease in pH, as Reaction (9) moves from left to right to establish equilibrium.<sup>(2)</sup> Any decrease in pH (whether it is caused by injection of a weak HAc or a strong acid such as HCl) always results in a decrease in the concentration of  $CO_3^{2^-}$  ions,  $c_{CO_3^{2^-}}$ , as Reactions (6) and (7) shift from right to left, in order to maintain equilibrium. This decreases the saturation level of FeCO<sub>3</sub> in

<sup>&</sup>lt;sup>(2)</sup> Conversely, when acetate is added as a salt (e.g., sodium acetate, NaAc, which almost completely dissociates) Reaction (8) will shift from right to left to form HAc and the pH would increase.



**FIGURE 11.** SEM image and the result of EDS analysis of the X65 steel specimen exposed to a 3 wt% NaCl solution at initial pH 6.3, 80°C, and 0.53 bar  $pCO_2$ , supersaturated with FeCO<sub>3</sub> (initial  $S_{FeCO_3}$  = 200) following injection of a buffered solution containing different amounts of undissociated HAc: (a) no addition of HAc, under stagnant condition, (b) 3 mM undissociated HAc, under stagnant condition (results of EDS analysis of the "bare" area between the prisms), and (c) 3 mM undissociated HAc, under stagnant condition (results of EDS analysis of a prismatic crystal).

0)

solution and once it falls below unity, dissolution of  $FeCO_3$  will happen as Reaction (3) moves from right to left. The dissolution of protective  $FeCO_3$  layers resulting from a decrease in pH caused by injection of HCI was investigated and quantified previously<sup>39</sup> and will not be further discussed here.

In this work, an attempt was made to investigate if there is an effect of HAc on integrity and protectiveness of  $FeCO_3$  corrosion product layers that goes beyond the effect of pH. Therefore, a buffered HAc solution was injected with the same pH as the main solution, and still the result was partial loss of the  $FeCO_3$  layer. Even if the injected HAc solution was adjusted to have the same pH as the main solution, a small pH decrease in the main solution was measured upon injection (Table 3). The reason for this pH decrease was a source of much debate and the most plausible explanation is related to the formation of a soluble ferrous acetate complex, primarily  $FeAc^+$ , according to:

$$Fe^{2+} + Ac^{-} \leftrightarrows FeAc^{+}$$
 (1)

Following injection of buffered HAc, the Ac<sup>-</sup> ions are consumed by this reaction, which moved from left to right; at the same time, due to consumption of Ac<sup>-</sup> ions, the HAc dissociation (Reaction [9]) also shifts from left to right in order to maintain equilibrium, which results in a pH decrease. Regardless, it was experimentally proven above that this small pH decrease that occurred when buffered HAc was injected into the main solution was not the main cause for the dissolution of the FeCO<sub>3</sub> layer (Figures 6 and 7). So, other possibilities were explored.

The same FeAc<sup>+</sup> forming Reaction (10) can be used to propose a different mechanism for dissolution of the FeCO<sub>3</sub> layer in the presence of HAc, following the ideas presented by Gulbrandsen.<sup>18</sup> As the Fe<sup>2+</sup> ions are consumed by Reaction (10) moving from left to right, the  $c_{Fe^{2+}}$  decreases and eventually can drop below the saturation limit, causing a dissolution of the FeCO<sub>3</sub> layer. The question is now whether this perfectly plausible explanation proposed by Gulbrandsen is actually true in



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**FIGURE 12.** SEM image of the cross-sectional view of the X65 steel specimen exposed to a 3 wt% NaCl solution at initial pH 6.3, 80°C, and 0.53 bar  $pCO_2$ , supersaturated with FeCO<sub>3</sub> (initial  $S_{FeCO_3}$  = 200) following injection of a buffered solution containing different amounts of undissociated HAc: (a) no addition of HAc and (b) 3 mM undissociated HAc, under stagnant condition. Electron diffraction pattern of (c) prismatic crystals (in [a]), and (d) prismatic crystal (in [b]).

this case, and if the FeAc<sup>+</sup> complex formed in sufficient quantities under the conditions of the present study in order to cause the dissolution of the FeCO<sub>3</sub> layer.

It is known that the stability of ferrous acetate complexes increases with temperature.<sup>40</sup> As reported by Palmer and Hyde,<sup>41</sup> the concentration of ferrous acetate complexes at room temperature is negligible, while at 100°C it becomes significant at pH > 5 and [ $\Sigma$ Ac<sup>-</sup>] > 10 mM. At even higher temperatures, e.g., 300°C, the various ferrous complexes can become the dominant ferrous species in solution. This includes the abovementioned FeAc<sup>+</sup> but also FeAc<sub>2</sub>, FeCl<sup>+</sup>, and FeOH<sup>+</sup>. However, the question is whether at 80°C (the temperature used in the present study), the concentration of these ferrous complexes became high enough to deplete the solution of Fe<sup>2+</sup> ions and lead to a dissolution of the FeCO<sub>3</sub> layer. Using the equilibrium relations provided by Palmer and coauthors,<sup>40-41</sup> it was calculated that the decrease in Fe<sup>2+</sup> ion concentration of

various ferrous complexes (FeAc<sup>+</sup>, FeAc<sub>2</sub>, FeOH<sup>+</sup>, and FeCl<sup>+</sup>) at 80°C was not more than 50%, so this would have decreased  $S_{FeCO_3}$  by a similar amount due to the limited availability of Fe<sup>2+</sup> ions. To put this into context, this is in the same range as the effect caused by the small decrease of pH due to buffered HAc injection (0.1 to 0.3 pH units) which caused a decrease of CO<sub>3</sub><sup>2-</sup> ion concentration ( $c_{CO_3^{2-}}$ ) and  $S_{FeCO_3}$  by 36% to 75%, respectively. The corresponding increase of the FeCO<sub>3</sub> solubility product (K<sub>sp</sub>) caused by the change of ionic strength (I) due to the injection of the buffered HAc solution (85 mM of total HAc), was estimated using Equation (5) to be no more than 17%, resulting in an equivalent decrease in  $S_{FeCO_3}$ .

It needs to be pointed out that the abovementioned effects on the integrity of  $FeCO_3$  layer caused by the small pH change and ionic strength were already included in the calculations of  $S_{FeCO_3}$  change presented in Table 3. If the effect caused by the formation of various ferrous complexes is now

added in, the  $S_{FeCO_3}$  numbers presented there will be approximately halved. This poses a problem: when all of the effects are included, in all cases the calculated saturation  $S_{\text{FeCO}_3}$  remains greater than unity, yet experiments showed that part of the FeCO<sub>3</sub> layer dissolved, and this does not sound plausible. Therefore, it is concluded that either the calculation of S<sub>FeCO</sub> is not accurate enough or there is yet another effect of HAc on the stability of FeCO<sub>3</sub> that is currently unknown. These are some of the challenges that are being currently tackled in the ongoing research efforts. When it comes to calculation of S<sub>FeCO<sub>2</sub></sub>, the most recent focus is on improving the accuracy of prediction of the FeCO<sub>3</sub> solubility product K<sub>sp</sub> in ideal and nonideal solutions. Also, there is an ongoing effort on building a more accurate water chemistry model to better predict the  $Fe^{2+}$  ion concentration ( $c_{Fe^{2+}}$ ) and the carbonate,  $CO_3^{2-}$  ion concentration ( $c_{CO_2^{2-}}$ ), by including the effects of complex species such as FeAc<sup>+</sup>, FeAc<sub>2</sub>, FeOH<sup>+</sup>, and FeCl<sup>+</sup>.

Irrespective, the data presented above seem to indicate that the FeCO<sub>3</sub> prismatic crystals were somewhat harder to dissolve than the FeCO<sub>3</sub> plates. For example, from Figure 3, it can been seen that almost all of the iron carbonate plates are gone after buffered HAc solution injection, leaving iron carbonate prismatic crystals behind. The prismatic crystals were not visible before the dissolution (Figure 3[a]). One explanation is that the prismatic crystals were hidden underneath the plates, as they formed closer to the steel surface. However, one should not ignore the possibility of Ostwald ripening, which refers to a spontaneous process of crystal enlargement which occurs because smaller crystals are kinetically favored (nucleate more easily however are less stable), while large crystals are thermodynamically favored (represent a lower energy state).42 Therefore, small crystals attain a lower energy state when transformed into larger crystals.

Regardless, it can also be observed from the results presented above that the larger FeCO<sub>3</sub> crystals (both plates and prisms) from the outer layer were preferably dissolved, when compared to the thin adherent inner layer of FeCO<sub>3</sub> that was much more resilient (i.e., more resistant to dissolution). One could speculate that this is somehow related to the favorable morphology of the inner layer, but another plausible explanation can be postulated. Even if the thin adherent inner layer of FeCO<sub>3</sub> was just as readily dissolved as the outer layer consisting of plates and/or prismatic crystals, it can be argued that it that was easier to "rebuild/repair." This is because of its location closer to the steel surface, where due to corrosion of the underlying steel substrate, the concentration of Fe<sup>2+</sup> ions was higher and the concentration of H<sup>+</sup> ions was lower (i.e., the pH was higher). Both factors contribute to having a higher saturation level of FeCO<sub>3</sub> in the inner layer, driving the rate of precipitation up and making it easier to rebuild/repair the damaged FeCO<sub>3</sub> layer. In the case of FeCO<sub>3</sub> formed on platinum, there was no corrosion of the substrate, hence the concentration of Fe<sup>2+</sup> ions in the thin adherent inner FeCO<sub>3</sub> layer was not any higher than elsewhere in the layer, however, the concentration of H<sup>+</sup> ions was still much lower (i.e., surface pH higher) due to the cathodic potential applied to the platinum substrate. This explanation is also consistent with the electrochemical measurements (Figures 9[a] and [b]) where it can be seen that after injecting the buffered HAc solution the corrosion potential suddenly decreased while the corrosion rate increased as the outer FeCO<sub>3</sub> layer dissolved and the FeCO<sub>3</sub> inner layer was damaged, only to see both the corrosion potential and corrosion rate recover as the inner FeCO<sub>3</sub> layer was rebuilt/repaired. The exception is seen in Figure 9(c), where the intense flow

introduced turbulent mixing and high rates of mass transfer, effectively decreasing the surface concentration of  $Fe^{2+}$  ions and the surface pH, by making them much closer to the bulk values, which made it difficult for the inner  $FeCO_3$  layer to be repaired, and the high corrosion rates persisted. The effect of flow has been observed previously even at lower velocities (100 rpm) than the one used in the current research (1,000 rpm).<sup>43-44</sup>

#### CONCLUSIONS

The following conclusions can be drawn:

➤ The corrosion product layer formed on both platinum and X65 steel, under the experimental conditions of this research, is FeCO<sub>3</sub>, which presents a double-layered structure. The morphology of the outer FeCO<sub>3</sub> crystals can be plate- or prism-like. The inner layer is more compact and adherent to the steel surface and is the key to the protective effect.

> It is shown that, under the experimental conditions of this research, an injection of a buffered HAc solution at the same pH can partially dissolve the  $FeCO_3$  layer, leading to an increase in the corrosion rate.

> The dissolution of  $FeCO_3$  by injection of a buffered HAc solution can be explained by the resulting pH drop, an increase in the ionic strength of the solution and the formation of ferrous acetate complexes, which all lead to a decrease in the  $FeCO_3$  supersaturation.

> The calculations of  $FeCO_3$  supersaturation are currently not accurate enough to properly account for this behavior, and improvements in the model are required.

> The dissolution of FeCO<sub>3</sub> seems to be selective, with the outer layer (FeCO<sub>3</sub> plates and prismatic crystals) dissolving easier. The inner FeCO<sub>3</sub> layer was not as affected and was readily repaired over the course of the experimentation leading to low final corrosion rates.

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