

## EFFECT OF ORGANIC ACIDS IN CO<sub>2</sub> CORROSION

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### ABSTRACT

In the majority of the published work related to organic acid corrosion of mild steel, the focus is on acetic acid due to its prevalence in a typical organic acid mix seen in the field. In this work, the electrochemical behaviour of X65 carbon steel in the presence of other important organic acids (formic and propionic) and the effect that these have in the growth and protectiveness of iron carbonate (FeCO<sub>3</sub>) scale have been investigated.

It was found that very little difference exists in electrochemical behaviour of the formic, acetic and propionic acids when it comes to CO<sub>2</sub> corrosion of mild steel, given that the pH and concentrations of the undissociated organic acids is the same. Just like the other two weak organic acids, formic acid increases the corrosion rate due to an additional cathodic reaction: direct reduction of undissociated formic acid; this reaction is very temperature sensitive and may be limited by diffusion. The presence of organic acids makes it harder for protective iron carbonate scales to form due to a “scale undermining” effect. The scale precipitation rate is not directly affected, however, the time it takes to reach low corrosion rates is.

**Keywords:** organic acid corrosion, formic acid, acetic acid, CO<sub>2</sub> corrosion, iron carbonate scale.

### INTRODUCTION

Weak organic acids such as formic acid, acetic acid and propionic acid are commonly found in oilfield brines. The organic acid content has been considered as one of the main causes of mild steel pipeline failures in some cases<sup>1</sup>. In oilfield pipelines with low pCO<sub>2</sub>, the corrosion issues are usually easily managed. However, when small amounts of organic acid are present, the corrosivity of the brine can change dramatically<sup>2</sup>. The vast majority of open literature on the effect of organic acids on CO<sub>2</sub> corrosion of mild steel focuses on acetic acid<sup>3,4,5</sup> as this acid usually dominates the mixture of organic

acids seen in the field. However, issues have been raised related to formic and propionic acids which are other commonly found organic acids in oilfield brines. In a rare published study, Olsen has reported that the presence of formic acid could cause dramatic corrosion issues in oilfield brines<sup>6</sup>. Acetic and propionic acids have very similar chemical characteristics while the formic acid is much more acidic, as shown by the tabulated  $pK_a$  values in Table 1. Whether this translates into different corrosivity is investigated in the present study and reported in the text below.

Protective iron carbonate scale can form on the steel surface depending on the water chemistry and temperature. If the concentrations of  $Fe^{2+}$  and  $CO_3^{2-}$  exceed the solubility limit, precipitation on the steel surface will begin and the  $FeCO_3$  scale will form. While the mechanisms and the kinetics associated with the  $FeCO_3$  scale formation have been extensively studied<sup>7,8</sup>, the influence of organic acids on the scale characteristics still lacks complete understanding as various and sometime contradictory opinions have been expressed<sup>6,9</sup>. In general, the protectiveness of the scale can vary: some scales being very protective; some unprotective; and others even leading to a localized corrosion process.<sup>10</sup> It is well established iron carbonate precipitation rate and the scale protectiveness is very dependent on the temperature and the pH<sup>11</sup>, however, how the presence of organic acids affects this process remains unclear. Some new evidence is presented below.

## EXPERIMENTAL PROCEDURE

A three-electrode setup was used in all the experiments and is shown in Figure 1. X65 carbon steel material was used for the rotating cylinder electrode (RCE), which served as the working electrode (WE). A concentric platinum ring was used as a counter electrode (CE) with a saturated silver-silver chloride (Ag-AgCl) as the reference electrode (RE). The pH was monitored with an electrode continually immersed in the electrolyte. Temperature was regulated using a thermocouple immersed in the solution and a controller linked to a hot plate.

The glass cells were filled with 2 liters of electrolyte, which was made from de-ionized water and 3 mass% NaCl. In all experiments,  $CO_2$  was continuously bubbled through the electrolyte for approximately 1 hour before the experimentation and during the entire experimental procedure. This was done in order to ensure that all the dissolved oxygen was removed and to maintain saturation with  $CO_2$  of the test solution. When needed, hydrochloric acid (HCl) or sodium bicarbonate ( $NaHCO_3$ ) was added to adjust the pH. The experimental temperature was maintained within  $\pm 1^\circ C$  in all experiments.

Before each polarization experiment, the steel WE surface was polished using 240, 320, 400 and 600 grit silicon carbide (SiC) paper, washed with alcohol, mounted on the specimen holder, and immersed into the electrolyte. The free corrosion potential was immediately measured. Polarization resistance ( $R_p$ ) measurements were conducted by polarizing the WE  $\pm 5mV$  from the  $E_{oc}$  (free corrosion potential) and scanning at  $0.1mV/s$ . The solution resistance was measured independently using alternating current (AC) impedance and the measured  $R_p$  then was corrected. AC impedance measurements were done by applying an oscillating potential ( $\pm 5mV$ ) around the  $E_{oc}$  to the WE using the frequency range of 1Hz to 100kHz.

Three sets of experiments were conducted to answer some rather specific questions:

- **Are there any significant differences in electrochemical behavior of various organic acids?**  
The first set of experiments was done with three different organic acids (formic, acetic and propionic) in order to observe the effect on the corrosion mechanism. The same undissociated

concentration of each organic acid was used under non-scaling conditions (pH 4, T=25°C, 1000rpm of rotating speed, 0.96bar of CO<sub>2</sub>). The total concentration and undissociated concentration of each organic acid is shown in Table 2. Cathodic and anodic potentiodynamic sweeps were conducted separately, and respectively, starting from the open circuit potential.

- **What is the mechanism of mild steel CO<sub>2</sub> corrosion in the presence of formic acid?**  
The second set of experiment was done to characterize in detail the electrochemical corrosion behavior of formic acid which appeared to be chemically distinctly different from the other two. Tests were conducted at different concentrations, pH, velocities, and temperatures. The total concentration of formic acid was varied from 100ppm to 5000ppm. The temperature varied from 25°C to 80°C. The rotational velocity varied from 1000 rpm to 4000 rpm, and the pH varied from 4 to 6. The corrosion rate was obtained using LPR and the corrosion mechanisms were studied by using potentiodynamic sweeps. The experimental conditions are summarized in Table 3.
- **Do organic acids affect the formation and protectiveness of iron carbonate scale?**  
The third set of experiments compares the effect of acetic and formic acid on iron carbonate scale formation. Three water chemistry conditions were tested in 10 days exposures (Table 4). One experiment was conducted without organic acid as a baseline for scale formation conditions in “pure” CO<sub>2</sub> corrosion. Two experiments were conducted for each of the organic acids at undissociated concentrations of 18 and 90 ppm (Table 5). All tests in this series were conducted at 80°C, 1 bar total pressure (0.56 bar pCO<sub>2</sub>, balance pH<sub>2</sub>O), 3wt% NaCl, pH 6.6 which was adjusted by adding a deoxygenated NaHCO<sub>3</sub> solution, initial Fe<sup>++</sup> 10 ppm, and a rotational velocity of 1000 rpm.

## RESULTS AND DISCUSSION

### **Are there any significant differences in electrochemical behavior of various organic acids?**

To compare the three different organic acids with respect to CO<sub>2</sub> corrosion, a reasonable course of action appears to be: first fix the solution conditions and then in separate experiments add the same quantity of a particular acid and proceed with the measurements. However, adding the same quantity of the acid would change the pH differently in the three cases (see pK<sub>a</sub> values in Table 1). Therefore, in order to isolate the effect of organic acid type and separate it from the effect of the respective acid strength, after a particular acid is added, the pH should be adjusted to the same value by using NaHCO<sub>3</sub>. On the other hand, it is well established for acetic acid that it is the *undissociated* organic acid in the solution which affects corrosion<sup>3,4</sup>. At the same pH, the undissociated concentration of the three acids would be different and a further adjustment of the water chemistry needs to be made which would enable meaningful comparisons of the effect on the corrosion rate. Therefore in all the corrosion experiments discussed below, both the pH and the undissociated concentration of the various acids in the solution were controlled. This was achieved by calculating the required total amount of organic acid (see Table 2) and NaHCO<sub>3</sub> that needed to be added to a CO<sub>2</sub> solution in order to achieve the same pH and the same undissociated acid concentration in each case. Figure 2 shows the potentiodynamic sweeps conducted during corrosion of mild steel in a pure CO<sub>2</sub> solution as well those conducted in comparable solutions containing an additional 85 ppm of undissociated organic acid (formic, acetic, and propionic respectively). The addition of 85 ppm of any of the acids clearly changed the corrosion process significantly by increasing the cathodic reaction and by possibly retarding mildly the anodic reaction, overall resulting in a higher corrosion rate. However, it is important to notice that the corrosion “behaviour” of the three organic acids is very similar. The anodic reaction was virtually identical for all three acids. The limiting current portions of the cathodic curves were also very close and the only observable difference is a small rate increase seen in the charge transfer portion of the cathodic curve in

the case of formic acid. This may result in a slightly higher corrosion rate of mild steel in formic acid when compared to the other two acids under the same conditions.

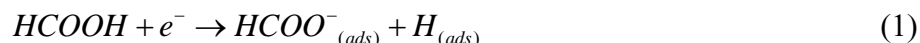
Therefore, based on the limited number of experiments, one can conclude that the answer to the question posed at the beginning of this section is: *there is very little difference in electrochemical behaviour of the formic, acetic and propionic acid when it comes to CO<sub>2</sub> corrosion of mild steel, given that the pH and concentrations of undissociated organic acids are the same.*

### **What is the mechanism of mild steel CO<sub>2</sub> corrosion in the presence of formic acid?**

To answer the question above, formic acid was tested for a range of conditions systematically, changing only one parameter at a time in a similar fashion as was done earlier for acetic acid<sup>3,4</sup>.

Effect of formic acid concentration. The effect of the formic acid concentration on CO<sub>2</sub> corrosion is shown in Figure 3 and Figure 4. The corrosion rate does not change very much up to 36 ppm of undissociated acid and then mildly increases as the concentration of formic acid increases (Figure 3). This is rather consistent with the behaviour of acetic acid where excess of 50 ppm was needed to overwhelm the corrosion action of carbonic acid (at 25°C and 1 bar CO<sub>2</sub> the concentration of carbonic acid is about 6 ppm)<sup>3,4</sup>.

The potentiodynamic sweeps shown in Figure 4 illustrate that the addition of formic acid increases significantly the limiting current for the cathodic species. Furthermore, at the high acid concentrations, a rather clear charge transfer region becomes distinct for the cathodic process. The rate of anodic iron dissolution does not seem to be affected much by the addition of the acid. Again these results are very similar to what was seen in the case of acetic acid,<sup>3,4</sup> and they corroborate the corrosion rate measurements shown in Figure 3. Addition of 36 ppm of undissociated formic acid does not change the corrosion rate or mechanism much. More acid seems to bring out a new charge transfer controlled cathodic reaction (direct reduction of HCOOH)



The mechanism for this reaction (“direct” reduction of the undissociated formic acid) is very similar to the direct reduction of other weak acids such as acetic acid or even carbonic acid. According to this reaction path, the concentration of formic acids affects the corrosion rate even at a constant pH, a fact experimentally proven in this study. This would not be the case if undissociated formic acid served only as a “source” of H<sup>+</sup> ions.

Effect of pH. With an increase in the pH, the corrosion rate diminishes (see Figure 5). The potentiodynamic sweeps shown in Figure 6 indicate that the anodic reaction is significantly accelerated particularly from pH4 to pH5, however, the cathodic reaction is slowed down at the same time, actually so much that the corrosion rate decreases. The reason for this behaviour of the cathodic reaction is the reduced availability of protons (H<sup>+</sup> ions) as well as the undissociated formic acid which dissociates to form formate with increased pH. As indicated in the small table imbedded in Figure 6, when 100 ppm of formic acid is added to the system, 36 ppm of undissociated formic acid is present at pH4 (the balance being formate), however this is reduced to only 0.5 ppm at pH6. As it is the undissociated acid which is responsible for corrosion, the reduction in the corrosion rate seen in Figure 5 is easier to understand.

Effect of flow. To investigate the effect of flow, rotation speed was varied. The corrosion rate increased very little as shown in Figure 7. The potentiodynamic sweeps shown in Figure 8 indicate that only the limiting current for the cathodic reaction was affected. The rate of increase of limiting current was consistent with a mass transfer mechanism. However, since neither the corrosion potential in Figure 8 nor the corrosion rate in Figure 7 changed much with the variation of velocity, this indicates that the corrosion process under these conditions is predominantly controlled by a charge transfer process. These results are qualitatively very similar to what was seen in the case of acetic acid.<sup>3,4</sup>

Effect of Temperature. A major change in the corrosion rate was seen with an increase in temperature, as illustrated in Figure 9. A pure CO<sub>2</sub> corrosion rate increases by a factor of 2-3 over the same temperature range, while in the presence of formic acid the corrosion rate increased more than tenfold. This is despite the fact that some of the acid might have been lost to the gas phase by evaporation. The very different temperature sensitivity (activation energy) is indicative of a different corrosion mechanism (reactions 2-7) which is due to a new cathodic reaction (1). Figure 10 illustrates how the temperature accelerates all the processes involved in the corrosion reaction. One should keep in mind that with the increase in temperature the partial pressure of water vapour increased which led to a reduction of the CO<sub>2</sub> partial pressure as indicated in the small imbedded table in Figure 10.

In answer to the question posted at the outset of this heading one can conclude that: *formic acid increases the corrosion rate due to an additional cathodic reaction: direct reduction of undissociated formic acid (1); this reaction is very temperature sensitive and may be limited by diffusion.*

### **Do organic acids affect the formation and protectiveness of iron carbonate scale?**

The baseline test with protective iron carbonate film formation in pure CO<sub>2</sub> corrosion (without organic acids) was conducted to record the change in the corrosion rate and the corresponding scale morphology and characteristics. At the beginning of the experiment, the corrosion rate on the bare steel surface was 1.5 – 2 mm/yr and decreased within a few days to a very low value (< 0.1 mm/y) as iron carbonate films formed (see Figure 11). The iron carbonate layer responsible for this reduction in corrosion rate is shown in Figure 12. A rather thin (5 – 10 μm) iron carbonate film can be observed consisting of cubic crystals densely packed together.

In the presence of 18ppm of acetic acid, it took about three days to reach the comparably low corrosion rates. With 18ppm of formic acid it took as long as five days to do the same. This would seem to suggest that the formation of a protective iron carbonate scale was retarded in the presence of organic acids. However, this conclusion is not supported by the SEM images shown in Figure 13 and Figure 15 where much more iron carbonate scale is seen than in pure CO<sub>2</sub> conditions (Figure 12). Actually the scale is twice as thick in the case of acetic acid (Figure 13) and up to five times thicker in the case of formic acid (Figure 15). Very rough calculations of the volumetric rate of formation suggest that, if anything, the rate of iron carbonate precipitation has increased and not decreased in the presence of organic acids. This observation and the fact that it took longer to form a protective scale can both be explained by considering the bare steel corrosion rate in the presence of organic acids. As organic acids increase the corrosion rate of bare steel increases when compared to pure CO<sub>2</sub> corrosion. It was harder for the iron carbonate film to take a foothold on a steel surface that kept corroding underneath at a higher rate. At the same time the corrosion process kept generating plenty of dissolved Fe<sup>2+</sup> which sustained the iron carbonate precipitation and hence more scale was observed. Clearly in the presence of formic acid this effect was more pronounced since formic acid is slightly more corrosive than acetic, as described in the sections above, and the film undermining effect was a bigger factor.

In a separate series of experiments, as the concentration of undissociated organic acids was increased from 0ppm to 90ppm, it took longer to reach the very low corrosion rates, because of the higher initial corrosion rate and the fact that the corrosion rate would increase to a maximum level before decreasing (Figure 11). Consequently the amount of scale formed on the steel surface was even larger: five to ten times more scale was found in the presence of 90 ppm acetic acid (Figure 14) and up to fifteen times more was recorded in the presence of 90 ppm of formic acid (Figure 16). This happened for the same reasons as explained above: high bare steel corrosion rates in the presence of organic acids made it more difficult for iron carbonate to form a protective layer on a rapidly corroding steel surface.

One can now answer the third and last question which this study addressed: *the presence of organic acids does not affect the rate of iron carbonate precipitation but does prolong the time it takes to form a protective scale due to a “scale undermining” effect.*

## CONCLUSIONS

- Very little difference was found in electrochemical behaviour of the formic, acetic and propionic acids when it comes to CO<sub>2</sub> corrosion of mild steel, given that the pH and concentrations of the undissociated organic acids was kept the same.
- Formic acid increases the corrosion rate due to an additional cathodic reaction: direct reduction of undissociated formic acid; this reaction is very temperature sensitive and may be limited by diffusion.
- The presence of organic acids, when it leads to an increased CO<sub>2</sub> corrosion rate, makes it harder for protective iron carbonate scales to form due to a “scale undermining” effect. The scale precipitation rate is not directly affected, however, the time it takes to reach low corrosion rates is.

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Table 1  
Physical and chemical properties of formic acid<sup>12, 13</sup>

	Formic acid	Acetic acid	Propionic acid
Formula	HCOOH	CH <sub>3</sub> -COOH	CH <sub>3</sub> -CH <sub>2</sub> -COOH
Molecular weight	46.03	60.05	74
Density, g/ml at 20°C	1.220	1.049	0.995
Melting point, °C	8.3	16.5	21
Boiling point, °C	100.8	118.1	141
Acidity (pK <sub>a</sub> )	3.75	4.76	4.88

Table 2  
Undissociated organic acids (acetic, formic and propionic acids), pH 4 and 25°C

R-COOH	Total concentration (ppm)	Undissociated acid (ppm)
Acetic Acid	100	85
Formic Acid	236	85
Propionic Acid	96	85

Table 3  
Experimental Conditions under no scale forming

Test solution	Water + 3 mass %NaCl
Test material	X-65
Temperature	25°C to 80°C
Total Pressure	1 bar CO <sub>2</sub>
Total [HFr]	0 to 5000ppm
pH	4 to 6
Rotation velocity	1000 to 5000rpm
Sweep rate	0.1 mV/s to 0.2 mV/s
Polarization resistance	From -5mV to 5mV (vs E <sub>oc</sub> )
AC Impedance	± 5mV vs. E <sub>oc</sub> from 1mHz to 100KHz
Potentiodynamic Sweep	From -600mV to 200mV (vs E <sub>oc</sub> )



Table 4

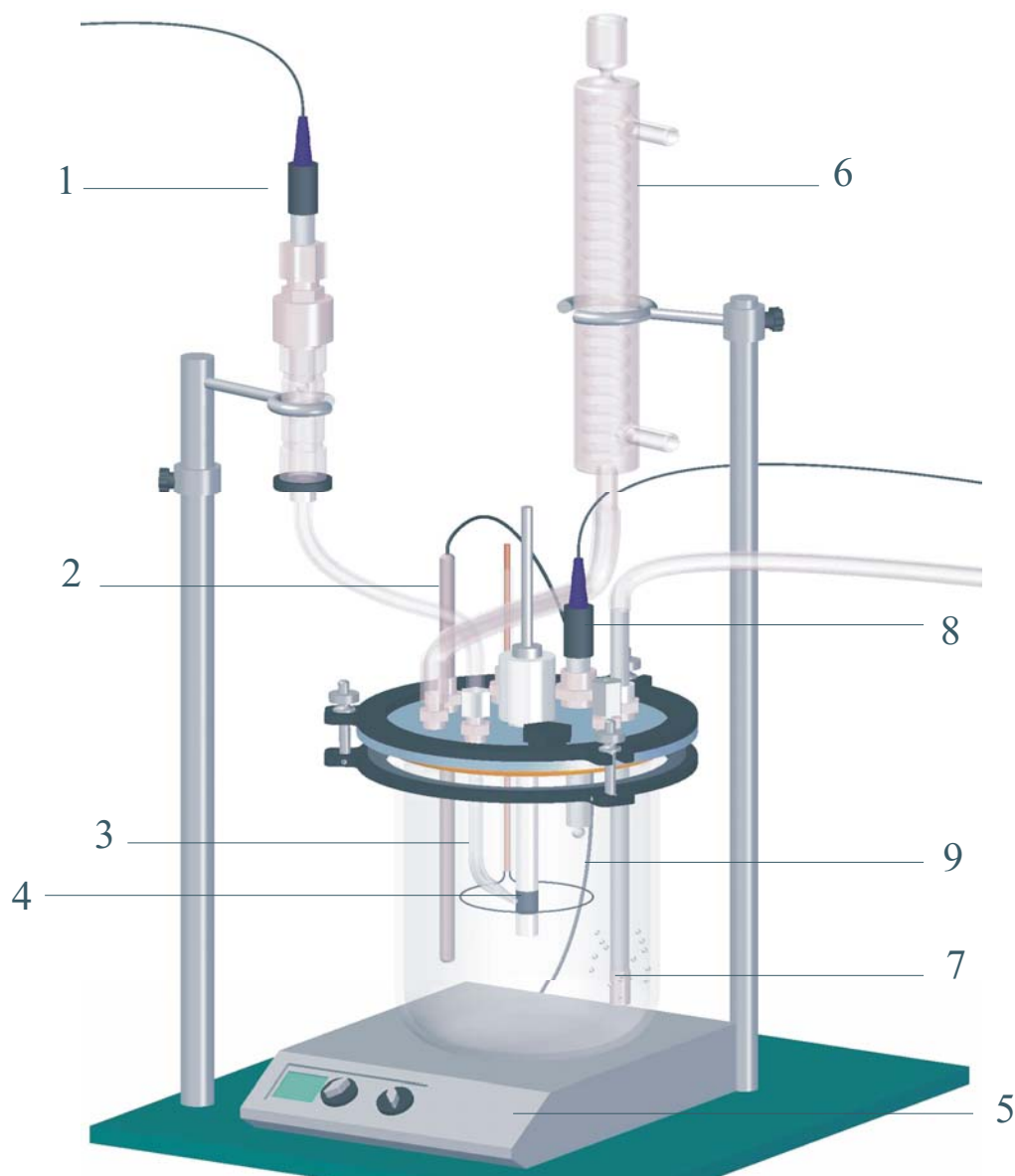
## Experimental conditions under scale forming

Test solution	Water + 3 mass %NaCl
Test material	X-65
Temperature	80°C
CO <sub>2</sub> Partial Pressure	0.56 bar CO <sub>2</sub>
Organic acids	Acetic acid & Formic acid
Undissociated (free) organic acid	18 and 90ppm
pH	6.6
Rotation velocity	1000rpm
Fe <sup>2+</sup> concentration	10ppm
Sweep rate	0.1 mV/s to 0.2 mV/s
Polarization resistance	From -5mV to 5mV (vs E <sub>oc</sub> )
AC Impedance	± 5mV vs. E <sub>oc</sub> from 1mHz to 100KHz

Table 5

## Undissociated organic acids (acetic acid and formic acid), pH 6.6 and 80°C

	Total organic acid (ppm)	Undissociated organic acid (ppm)
Acetic acid	1000	18
Formic acid	10110	18
Acetic acid	5000	90
Formic acid	50550	90



1. Reference electrode; 2. Temperature; 3. Luiggin Capillary; 4. Working electrode; 5. Hot plate; 6. Condenser; 7. Bubbler for gas; 8. pH electrode; 9. Counter electrode

Figure 1. Experimental cell design

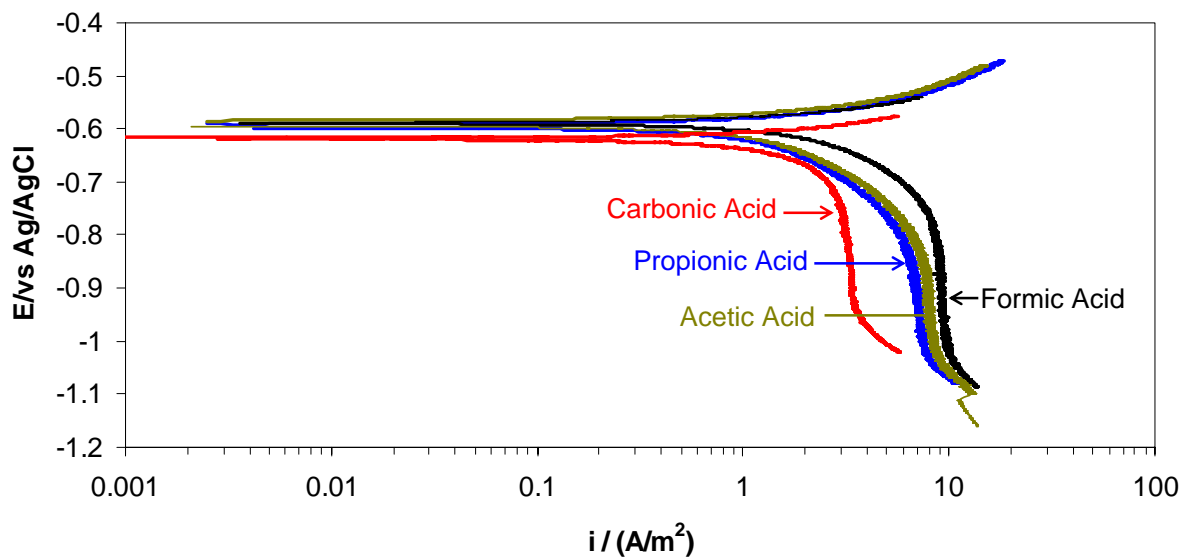


Figure 2. Potentiodynamic sweeps for 85ppm of each undissociated organic acid (acetic, formic & propionic), at pH 4, 25°C, 1000rpm.

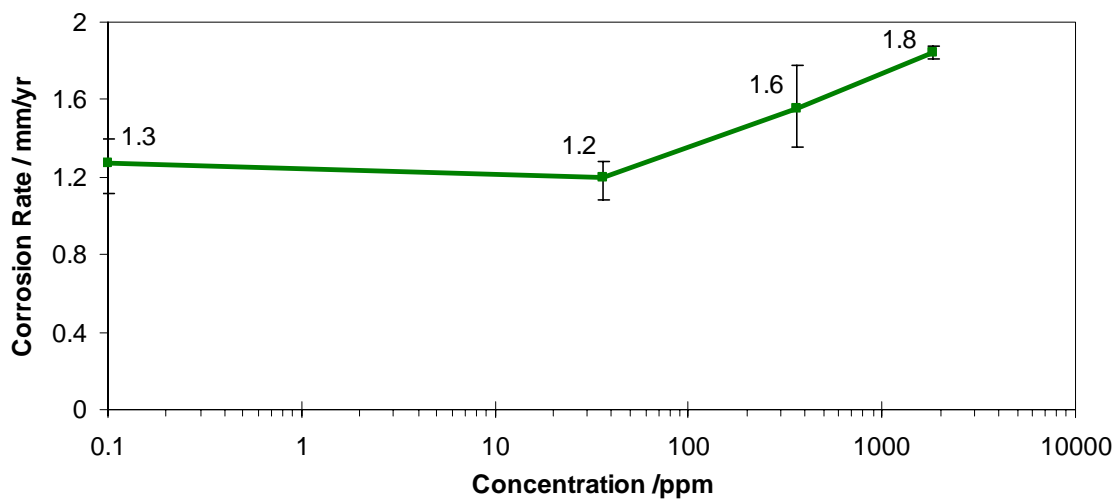


Figure 3. Effect of undissociated formic acid concentration on the corrosion rate of X-65 steel (3% NaCl,  $p\text{CO}_2=0.96\text{bar}$ , pH 4,  $T=25^\circ\text{C}$  and 1000rpm). Error bars represent the maximum and minimum experimental values.

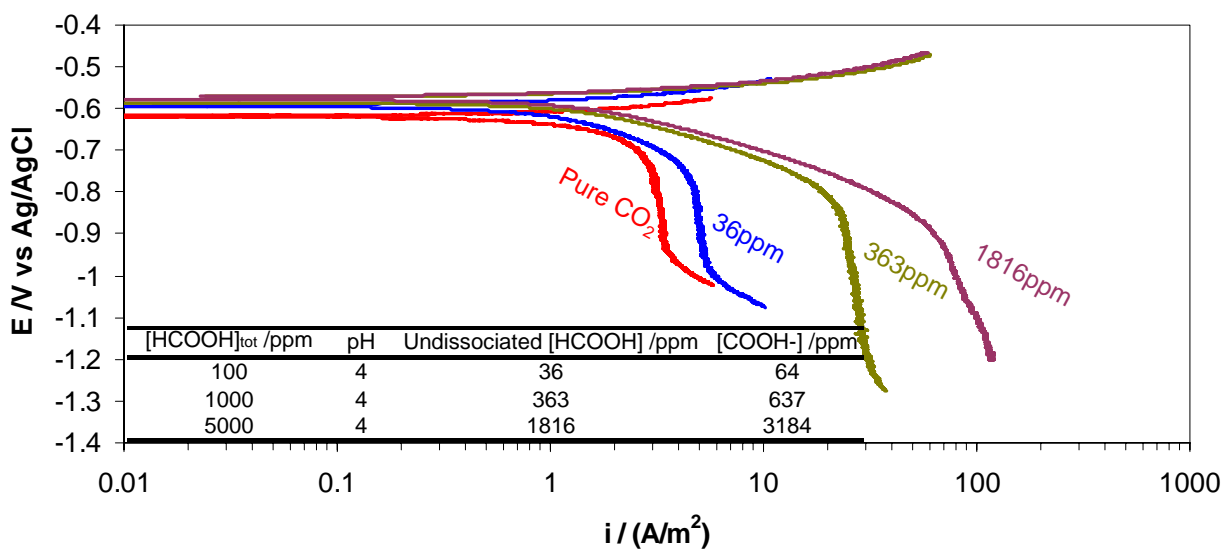


Figure 4. Potentiodynamic sweeps for X-65 steel (3% NaCl,  $p\text{CO}_2=0.96\text{bar}$ , pH 4,  $T=25^\circ\text{C}$  and 1000rpm).

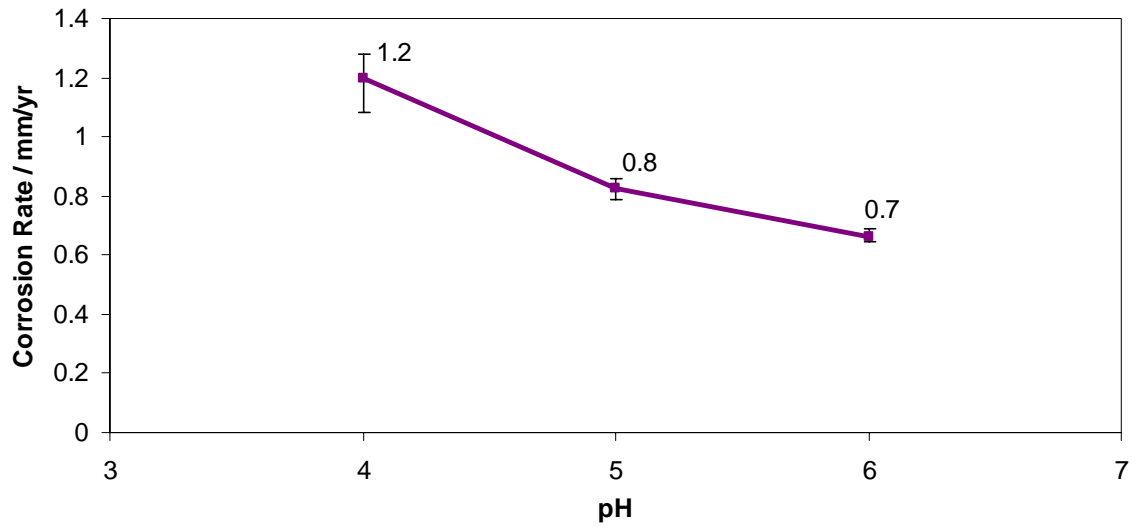


Figure 5. pH effect on the corrosion rate of X-65 steel (3% NaCl,  $p\text{CO}_2=0.96\text{bar}$ ,  $[\text{HCOOH}]_{\text{tot}}=100\text{ppm}$ ,  $T=25^\circ\text{C}$  and 1000rpm). Error bars represent the maximum and minimum experimental values.

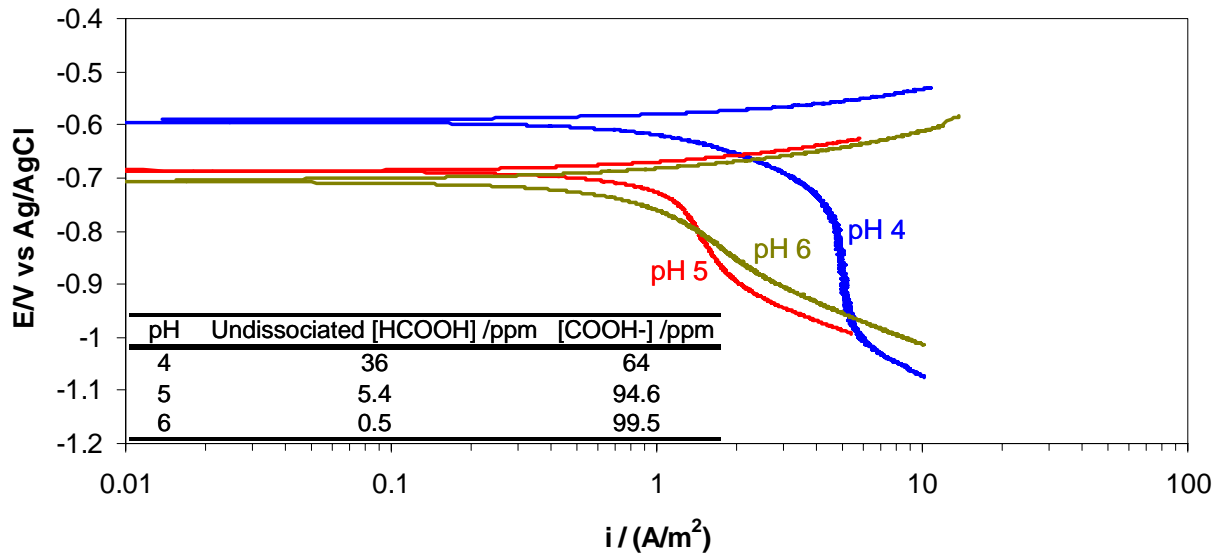


Figure 6. Potentiodynamic sweeps for X-65 steel (3% NaCl,  $p\text{CO}_2=0.96\text{ bar}$ ,  $[\text{HCOOH}]_{\text{tot}}=100\text{ppm}$ ,  $T=25^\circ\text{C}$  and 1000rpm).

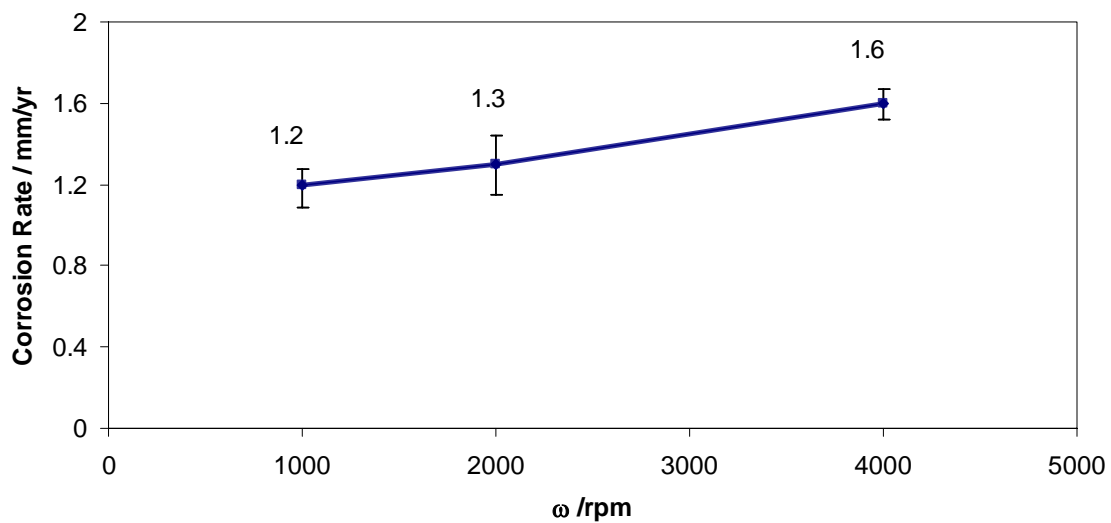


Figure 7. Rotational velocity effect on the corrosion rate of X-65 steel with 36ppm of undissociated formic acid concentration (3% NaCl,  $p\text{CO}_2=0.96$  bar, pH 4,  $[\text{HCOOH}]_{\text{tot}}=100$ ppm and  $T=25^\circ\text{C}$ ). Error bars represent the maximum and minimum experimental values.

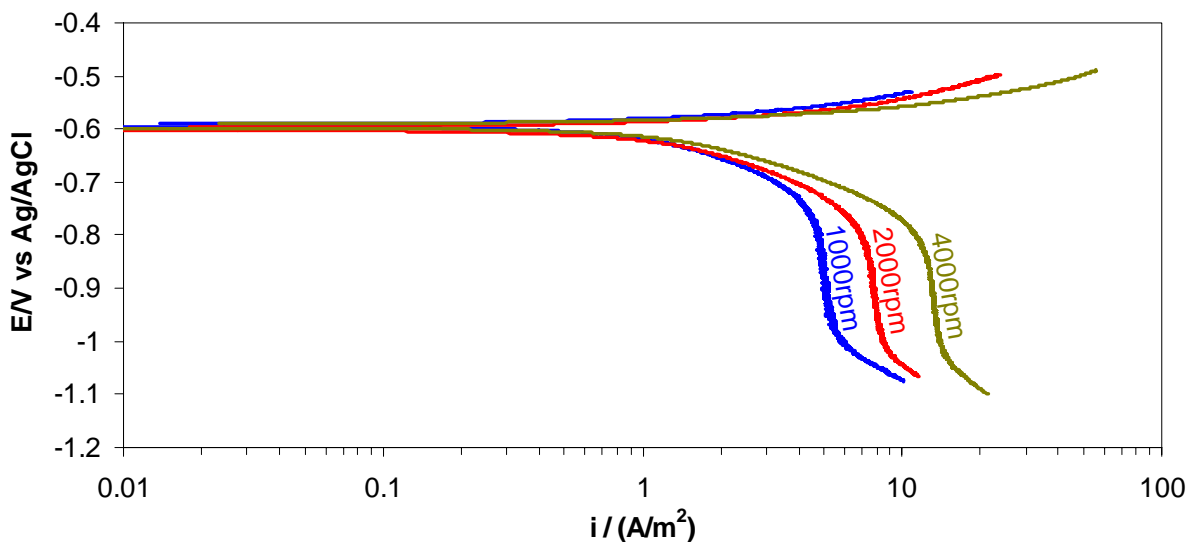


Figure 8. Potentiodynamic sweeps for X-65 steel with 36ppm of undissociated formic acid concentration (3% NaCl,  $p\text{CO}_2=0.96$ bar, pH 4,  $[\text{HCOOH}]_{\text{tot}}=100$ ppm and  $T=25^\circ\text{C}$ ).

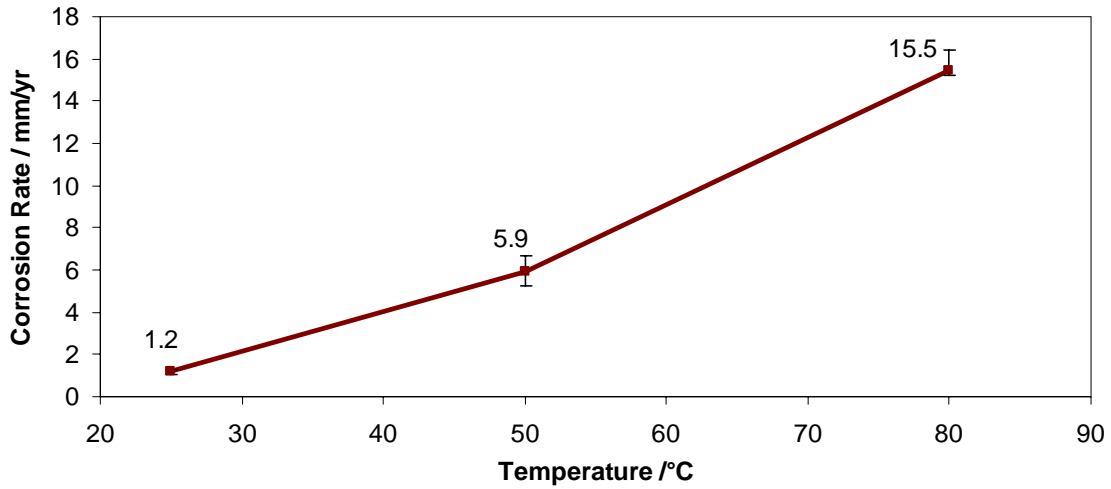


Figure 9. Temperature effect on the corrosion rate of X-65 steel (3% NaCl,  $p\text{CO}_2=0.96\text{bar}$ , pH 4,  $[\text{HCOOH}]_{\text{tot}}=100\text{ppm}$  and 1000rpm). Error bars represent the maximum and minimum experimental values.

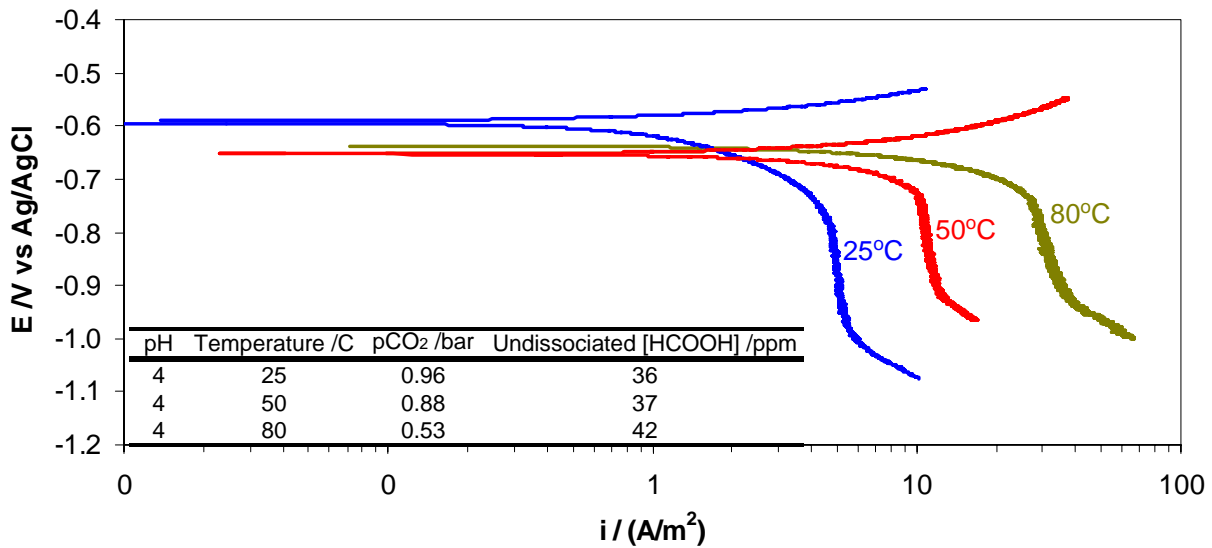


Figure 10. Potentiodynamic sweeps for X-65 steel (3% NaCl,  $p\text{CO}_2=0.96\text{bar}$ , pH 4,  $[\text{HCOOH}]_{\text{tot}}=100\text{ppm}$  and 1000rpm)

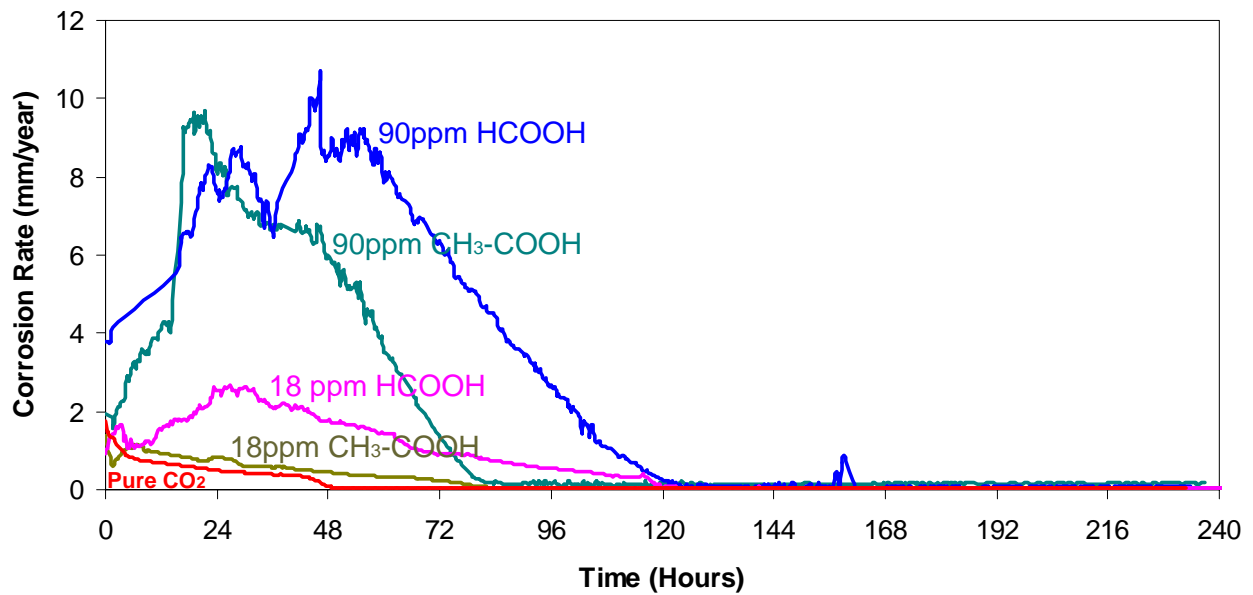


Figure 11. Undissociated acetic acid and undissociated formic acid effect on the corrosion rate of X-65 steel, bubbling CO<sub>2</sub> solutions, during 240 hours of exposure (3% NaCl, pH 6.6, 1000rpm and T=80°C).



Figure 12 . Baseline experiment without in pure CO<sub>2</sub> solution after 240h of exposure (pCO<sub>2</sub> =0.56 bar, pH 6.6, T=80°C). a) FeCO<sub>3</sub> scale morphology, frontal view and b) FeCO<sub>3</sub> scale thickness, cross section.



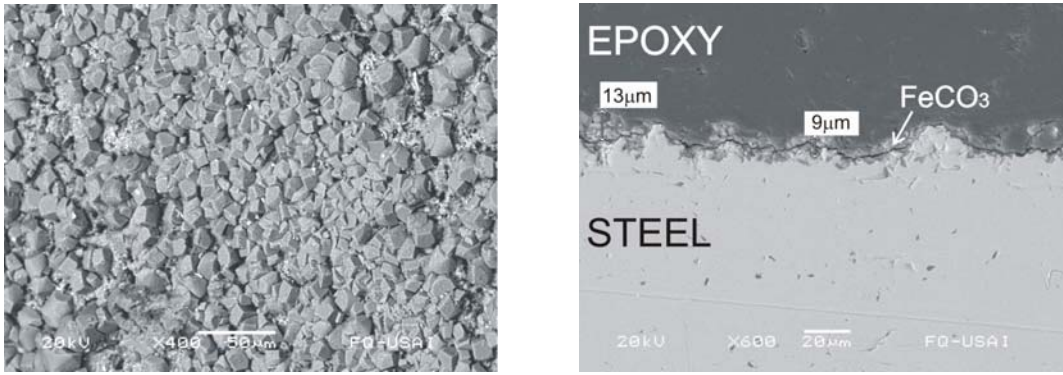


Figure 13. Carbon steel exposed at 18ppm of undissociated acetic acid after 240h of exposure ( $p\text{CO}_2 = 0.56$  bar, pH 6.6,  $T=80^\circ\text{C}$ ). a)  $\text{FeCO}_3$  scale morphology, frontal view and b)  $\text{FeCO}_3$  scale thickness, cross section.

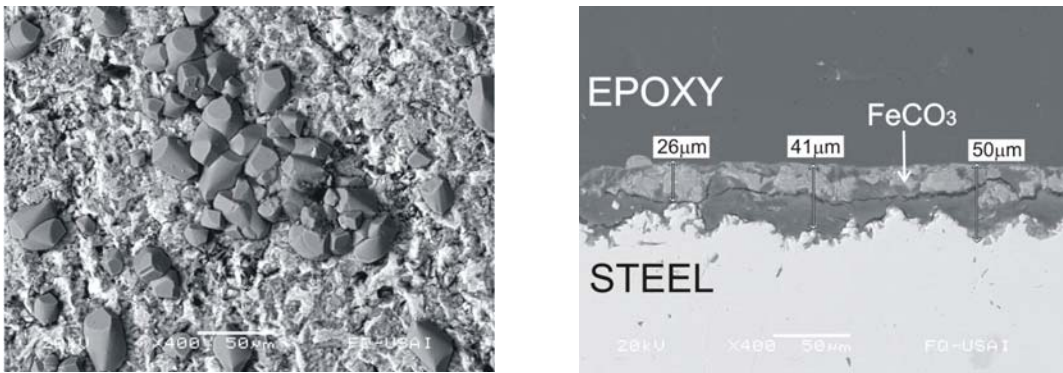


Figure 14. Carbon steel exposed at 90ppm of undissociated acetic acid after 240h of exposure ( $p\text{CO}_2 = 0.56$  bar, pH 6.6,  $T=80^\circ\text{C}$ ). a)  $\text{FeCO}_3$  scale morphology, frontal view and b)  $\text{FeCO}_3$  scale thickness, cross section.

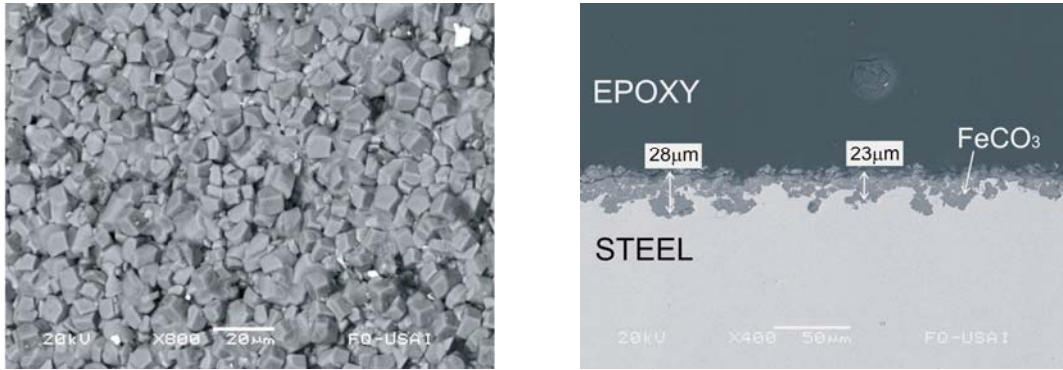


Figure 15. Carbon steel exposed at 18ppm of undissociated formic acid after 240h of exposure ( $p\text{CO}_2 = 0.56$  bar, pH 6.6,  $T=80^\circ\text{C}$ ). a)  $\text{FeCO}_3$  scale morphology, frontal view and b)  $\text{FeCO}_3$  scale thickness, cross section

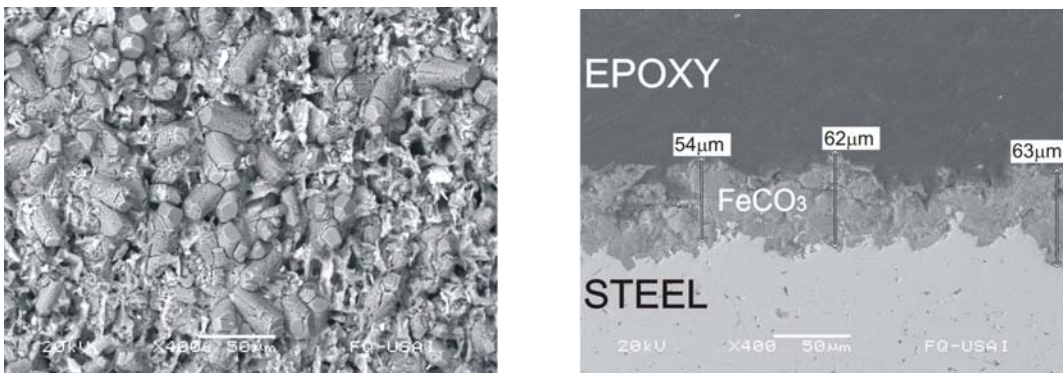


Figure 16. Carbon steel exposed at 90ppm of undissociated formic acid after 240h of exposure ( $p\text{CO}_2 = 0.56$  bar, pH 6.6,  $T=80^\circ\text{C}$ ). a)  $\text{FeCO}_3$  scale morphology, frontal view and b)  $\text{FeCO}_3$  scale thickness, cross section.