

Film Formation in CO₂ Corrosion with the Presence of Acetic: An Initial Study

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Formation of protective iron carbonate films in CO₂ corrosion can reduce corrosion rate substantially and the effects have been incorporated in various prediction models. The CO₂ corrosion with the presence of free acetic acid is known to increase corrosion rate below scaling temperature. The possible interaction between the formation of iron acetate and iron carbonate films can affect the protectiveness of the film. The study is done using 3% NaCl solution under stagnant CO₂ -saturated condition at the scaling temperatures at various pH values and HAC concentrations. The result show that the presence of HAC does not affect the formation of protective iron carbonate film but delays the attainment of protective iron carbonate due to a possibility of solubilising of ferrous ions and thinning of the films.

Keywords : CO₂ corrosion, acetic acid, film formation, iron carbonate film

1. Introduction

In any oil and gas exploration and production (E&P) project, detailed evaluation of all possible corrosion risks is done as part of a corrosion design basis memorandum of the project. This eventually forms the basis of material selection in the design stage and then provides inputs for maintenance and inspection strategies in the operation stage. The default material is always carbon steel, for low to medium corrosion rates as determined by CO₂ predictive models, with the option to include corrosion allowances and to deploy corrosion inhibitor. Since carbon and low alloy steels are extensively used in offshore and onshore oil and gas installations, accurate predictions of the corrosion rates of these materials in CO₂ environments are required. Many factors influence the chemistry of both the formation and dissolution of the corrosion products, the rates of chemical reactions, and the rates of transport of species involved in the corrosion. The electrochemical reactions are often accompanied by the formation of films of FeCO₃ (and/or Fe₃O₄) which can be protective or non-protective depending on the conditions under which they are formed.¹⁾ The precipitation of FeCO₃ is favoured with increase in pH, temperature and all measures that can reduce the transport of reactants and corrosion products from the steel surface.²⁾ Videm et al.³⁾ stated that,

reliable scales are often found above 80°C where as below this temperature, a pH value of at least 6 is required.

The prediction becomes complicated with the presence of acetic acid in CO₂ system. It is believed the presence of acetic acid species in the bulk solution acetic acid could diffuse to the surface and corrosion films and interfere in the FeCO₃ film formation. Since prediction of CO₂ corrosion is influenced by the formation of the protective film, the interaction between FeCO₃ and FeAc₂ must be understood. Crolet⁴⁾ highlighted that any replacement of bicarbonate by an equivalent amount of acetate will decrease the protectiveness of the corrosion layer due to the increase the local solubility of iron and elimination of alkalinity. In addition, the internal acidification which provides a local acetate-rich environment would trigger localised corrosion of the steel.

2. Experimental methodology

Electrochemical studies were performed under stagnant and low-flow conditions with the use of static electrodes. The test assembly consists of a standard one-litre glass cell with 3% NaCl solution that was saturated with CO₂ by purging for at least one hour prior to the exposure of an electrode. The pH of the solution could be adjusted by adding an amount of 1 M NaHCO₃. The pH value was checked by microcomputer pH-meter HANNA Instruments Model HI 8424, which had been calibrated using

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standard buffer solutions. The required test temperature was set through a hot plate. The electrochemical measurements were based on a three-electrode system, using a commercially available potentiostat with a computer control system. The reference electrode used was a saturated calomel electrode (SCE) (+0.242 V-SHE) and the auxiliary electrode is a platinum electrode. Corrosion rates were calculated based on the Linear Polarisation Resistance (LPR) method. The working electrode was prepared from commercial mild steel cylindrical rod with 0.785 cm² cross sectional area. The sample was spot welded with nickel-chromium wire and mounted in araldite resin. The sample surface was then progressively polished to 800-grade finish using silicon carbide papers. The specimen was de-greased and rinsed with ethanol and deionised water prior to immersion. Reproducibility of the results was ensured by accurate preparation of test samples and test solutions. The tests were repeated at least twice for each case. An

amount of acetic acid and acetate added was determined by the Handerson-Hasselbach equation in order to maintain the pH of the test solution. A concentration of 360

3. Results

3.1 General CO₂ corrosion trend with acetic acid

The effect of the 360 ppm acetic acid (HAc) and acetate (Ac) on the corrosion rate of mild steel in NaCl saturated with CO₂ at pH values of 3.8, 5.0, 5.5 and 6.0 tested at different temperatures is shown in Fig. 1 below.

Table 1. Concentration of HAc and Ac for 360 ppm

Species	Concentration of each specie at different pH			
	pH 3.8	pH 5.0	pH 5.5	pH 6.0
HAc	300 ppm	120 ppm	60 ppm	20 ppm
Ac	60 ppm	240 ppm	300 ppm	340 ppm

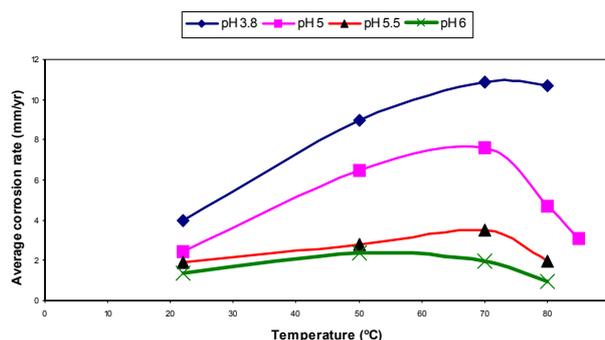
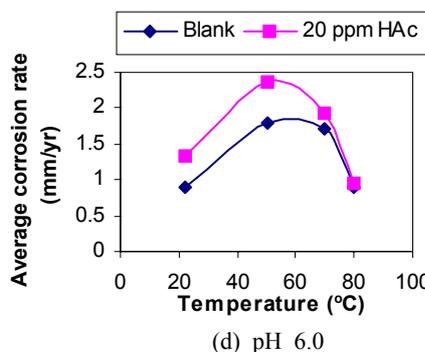
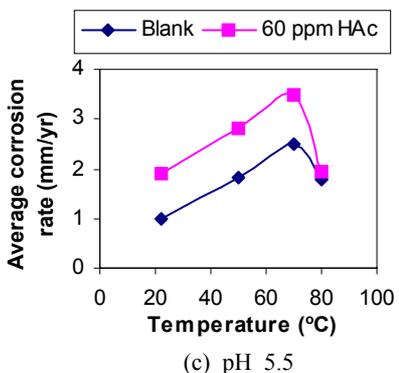
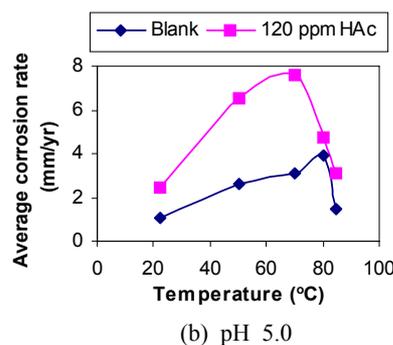
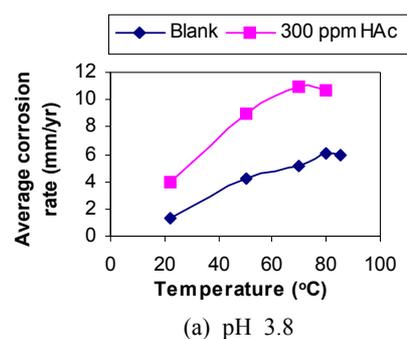


Fig. 1. Average corrosion rate of mild steel in NaCl saturated with 1 bar CO₂ with 360 ppm acetic acid species at various pH values and different temperatures.



Figs. 2(a-d). The effect of HAc on the corrosion rate of mild steel in NaCl saturated with 1 bar CO₂ at various pH values and different temperatures compared to the blank solution.

pm acetic acid species represents an amount of individual species at a certain pH as shown in Table 1 below.

This effect of the HAc at a particular pH is compared with the results of the blank CO₂ solutions as shown in Fig. 2(a-d) below.

Corrosion rate increases with the addition of acetic acid species to the solution. The increase is dependent on the concentration of free acetic acid at each pH value.⁵⁾ The corrosion rate also increases with temperature and reaches maximum values at the scaling temperatures (Ts) for pH 5, pH 5.5 and pH 6.0. Beyond the scaling temperatures, the corrosion rates decrease to low values. However, the decrease in corrosion rate is not distinctly observed for pH 3.8 since the test was only done up to 85°C, which indicates the scaling temperature is higher than 85°C.

3.2 The effect of acetic acid above Ts

Above scaling temperature, a protective corrosion film forms and the corrosion rate decreases gradually to a low value for both test solutions as summarised in Table 2 below.

The scaling temperatures for all pH values are not affected by the presence of acetic acid species. However, the attainment of the stable protective film is delayed as can be seen for example at pH 5.5 and 75°C as shown

in Fig. 3 below.

The time taken to form protective film ranges from 20 to 25 hours depending on the temperature and pH of the solution. When substantial protective film forms, the corrosion rate is reduced to approximately the same value of those of blank CO₂ solutions.

3.3 Effect of HAc on film formation

The behaviour of the CO₂ corrosion process with the presence of the HAc, above the scaling temperature at different pH values, can be inspected from the Fig. 4, 5 and

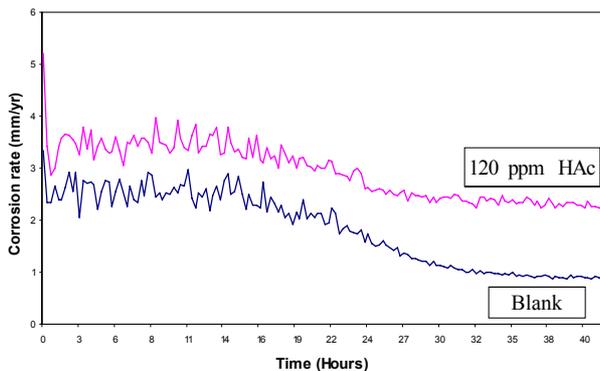


Fig. 3. Delay in protective film formation due to the presence of acetic acid at pH 5.5 and 75°C.

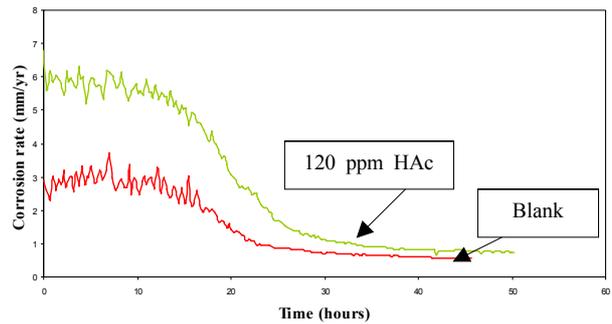


Fig. 4. Effect of acetic acid species on film formation at 85°C and pH 5.0.

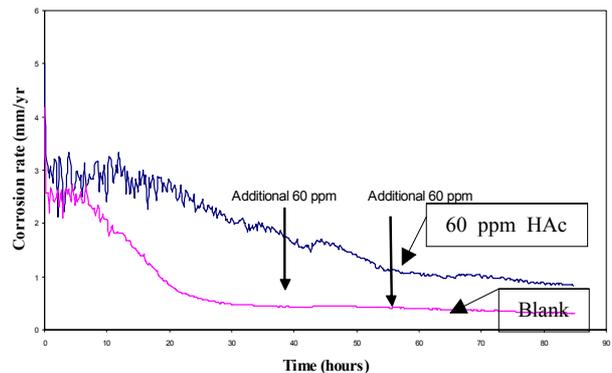


Fig. 5. Effect of acetic acid species on film formation at 80°C and pH 5.5.

Table 2. The effect of acetic acid on corrosion rate above scaling temperature.

Test Solution	Stage of Film Formation	Corrosion Rate above Scaling Temperature (mm/yr)				
		pH 5.0		pH 5.5		pH 6.0
		85°C	75°C	80°C	70°C	80°C
CO ₂ only	Initial	2.5	2.5	2.3	1.9	1.6
	Final	0.6	0.9	0.4	1.2	0.3
CO ₂ + 60 ppm HAc	Initial	5.6	3.5	2.9	2.0	1.6
	Final	0.7	2.3	1.0	0.3	0.3

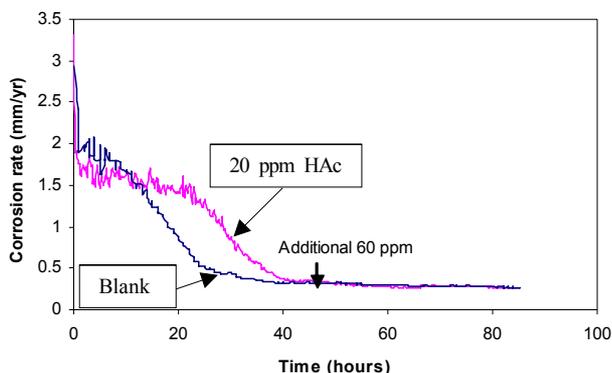


Fig. 6. Effect of acetic acid species on film formation at 80 °C and pH 6.0.

Table 3. Time taken to attain stable protective film formation

	pH 5.0	pH 5.5	pH 6.0
Blank	20 hours	20 hours	25 hours
360 ppm HAc/Ac	25 hours	50 hours	40 hours

6 below. Corrosion rates reduced to low values once protective films formed. Once the protective film forms, the addition of HAc as shown in the figures does not change the kinetics of the corrosion.

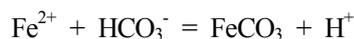
The time taken for the stable film to form for blank and HAc/Ac containing solutions differs. There is no drastic change in time taken for the blank solutions with the increase of the pH values. However, it is found that for the solutions containing 360 ppm HAc/Ac, the time taken increases to 25 hours, 50 hours and 40 hours respectively for pH 5, 5.5 and 6. This is summarised in Table 3 below.

4. Discussions

Iron carbonate film growth depends primarily on the precipitation rate. High pH results in a decreased solubility of iron carbonate, an increase in super saturation and consequently higher precipitation rate and surface scaling tendency. This applies to both solutions with and without the presence of acetic acid. Nonetheless, with the presence of acetic acid, competition between iron carbonate and iron acetate delays film formation below T_s and thins the film above T_s .

It is concluded by Nyborg⁶⁾ that the effect of protective corrosion films on the predicted corrosion rate varies between models. For example, NORSOK considers the effect of protective corrosion films more than de Waard models. It is apparent that NORSOK predicts lower corrosion rates model at high temperature and high pH than the de Waard model.

Below scaling temperature and without the presence of acetic acid, the film formed is not protective. The formation of iron carbonate (FeCO₃) can be represented by:



Acetic acid solubilises the ferrous ion (Fe²⁺) in the iron carbonate (FeCO₃) corrosion film promoting formation of iron acetate film, which is known to be soluble and hence not protective. We believe that below the scaling temperature, the thinning effect as proposed by Hedges⁷⁾ is not dominant as a film is not fully formed. This is evident in the invariant scaling temperature with or without acetic acid present in the system.

5. Conclusions

(1) Acetic acid/acetate does not alter the scaling temperature at the respective pH values but delays the attainment by 5-20 hours.

(2) Beyond the scaling temperature, the thermodynamics and kinetics of protective film formation competes with the thinning effect from solubilising of ferrous iron by acetic acid and delays the formation of the protective film.

6. Future work

The formation of surface film is important in CO₂ corrosion of carbon steel and low alloy steels since this can influence the corrosion control methodology. The iron and carbonate ions concentrations and other environmental parameters such as pH, affect precipitation kinetics of FeCO₃ film. Once the film is nucleated, the subsequent formation and growth are dependent on temperature of the solution. Based on the open literature, the corrosion films formed in CO₂ - containing solution can be of different morphology and thickness consisting of iron carbide (Fe₃C) and iron carbonate (FeCO₃) films. The presence of acetic acid solubilises the ferrous ions and delays the formation of protective FeCO₃ films below the scaling temperature. Furthermore, the suggestion that acetic acid thins the FeCO₃ films above scaling temperature is also feasible. Thus, the interaction of iron acetate and iron carbonate films in the CO₂ corrosion requires further studies to explain the observations from the current study. The studies of the interaction of surface films can be conducted by the use of Scanning Electron Microscopy (SEM), AFS and other visual morphological methods. SEM and metallurgical microscopy can be used to examine surface morphology. X-ray Diffraction (XRD) and X-ray Photoelectron Spectroscopy (XPS) can be used to identify the

structure and composition of the films.

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