

Role of acetic acid on the kinetics and mechanism of carbon steel dissolution under CO₂ top of line corrosion

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ABSTRACT

Based on a review of both literature and field data, it is apparent that the role of acetic acid (HAc) in oilfield brines is both extremely complex and somewhat controversial. Although it is commonly believed that the presence of this organic compound enhances both the general and the localized corrosion rate of carbon steel, HAc has recently been reported to also act as a weak inhibitor in specific aqueous environments. These observations prompted a study into whether such behavior is apparent in a CO₂ top of line corrosion (TLC) scenario i.e. when HAc dissolves into condensed water which forms on the upper internal wall of carbon steel pipelines during wet-gas or stratified flow. Four different water condensation rates/temperature TLC conditions were selected to investigate the role of HAc on both the kinetics and mechanism of carbon steel dissolution. A miniature three-electrode setup was developed to characterize the real-time TLC response through the implementation of electrochemical measurements. Surface analysis techniques (microscopy and profilometry) were performed to complement the electrochemical results. Collective consideration of the corrosion response and condensate chemistry indicates that similar effects were observed compared to those reported in the literature in bulk aqueous environments, in that the introduction of HAc can result in either an accentuation or diminution in corrosion rate depending upon the operating conditions. In fact, a decrease in corrosion rate was reported at a surface temperature of 20.5°C and water condensation rate of 0.5 ml/m².s despite a reduction in condensate pH being generated due to HAc presence.

Key words: top of line corrosion, acetic acid, sweet corrosion, CO₂

INTRODUCTION

Top of line corrosion (TLC) is a specific corrosion mechanism observed in the oil and gas industry. This phenomena occurs under stratified or wet-gas flow regimes when the upper internal pipeline walls are sufficiently cooled (by heat transfer to the surrounding outer environment), promoting local condensation of water vapor. Carbon dioxide (CO₂) and organic acids dissolving into the condensed water generate a change in the solution chemistry, ultimately influencing the corrosion kinetics of the contacting carbon steel.

In the oil and gas industry, the majority of hydrocarbon reservoirs produce both acid gases and volatile organic acids in conjunction with formation brine and hydrocarbons. These gases and volatile compounds create highly corrosive condensate chemistries in the context of carbon steel pipelines.

Organic acids such as acetic acid (HAc) are well known to accentuate TLC of carbon steel dramatically across a range of conditions, with their role receiving significant research attention. However, the underlying mechanism has not been explored extensively until the 2000s.¹ The influence of HAc on CO₂ corrosion needs to be studied holistically, as it can have a multitude of roles. These include, increasing the cathodic reaction rate (via lowering solution pH and through HAc providing a 'buffering' effect at the steel surface), inhibiting the anodic and cathodic charge-transfer reactions, and changing the solubility and protective characteristics of corrosion products.^{2,3,4}

Interestingly, some studies have shown that in specific bulk fluid chemistries under dynamic conditions, the effect of HAc addition can be minimal in terms of influencing the corrosion rate of carbon steel, even resulting in a diminution in general corrosion rate for a given fixed solution pH. Such observations have been attributed to the suppression of the anodic dissolution reaction and cathodic charge-transfer reaction due to the ability of HAc to adsorb onto the metal surface.^{4,5,6,7}

This study investigates whether, under certain conditions, HAc can also have a negligible effect on corrosion of carbon steel in specific TLC environments, despite being dosed at comparable field concentrations.

Based on previous studies on the role of HAc in CO₂ TLC conditions, a set of lab-scale experiments and conditions are devised here, consisting of four different water condensation rates and temperature combinations commonly reported or evaluated in TLC cases. For this purpose, a real-time corrosion monitoring setup⁸ was implemented in order to evaluate the transient corrosion response throughout experiments, and evaluate the role of HAc across a range of environments.

EXPERIMENTAL PROCEDURE

In the present study, mass loss and electrochemical test specimens were used in order to obtain corrosion rate data. The mass loss specimens consisted of cylindrical coupons 10 mm in diameter and 6 mm thick, with an exposed area to the vapor phase of 0.785 cm². Both mass loss and electrochemical specimens were manufactured from the same API 5L X65 carbon steel stock bar, which possessed a ferritic-pearlitic microstructure.

The miniature electrode setup used to monitor the changes in corrosion rate throughout the course of the experiment consisted of three metallic electrodes mounted inside the same geometry as the mass loss specimens (to ensure comparable heat-transfer to both specimen configurations). The working electrode consists of a 1 mm diameter X65 steel pin. The reference and counter electrodes both comprised of a 1 mm diameter Hastelloy® c276†(UNS N10276) wire as shown in Figure 1. Each electrode is individually isolated by a lacquer coating and a shrink wrap tube. It is worth noting that the use of the solid-state

† Trade name

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reference and counter were evaluated in a bulk solution with carbon steel and compared to results from a conventional three-electrode cell (platinum counter and Ag/AgCl reference electrode). The use of the miniature setup produced comparable results to the conventional three-electrode setup in solution chemistries indicative of the condensate produced in these TLC experiments.

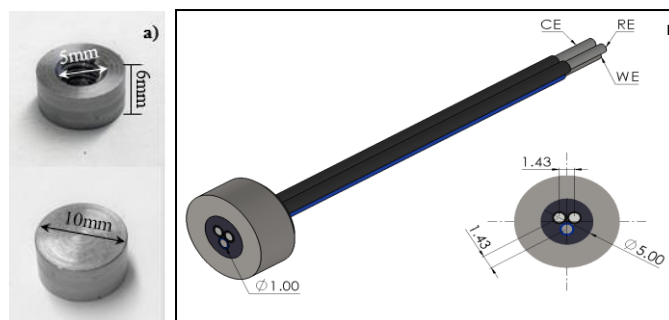


Figure 1: a) Mass loss specimens and b) the developed miniature electrodes consisting of two UNS N10276 wires as reference and counter electrodes and a X65 steel wire, isolated and flush mounted inside a larger X65 specimen (modified from Folea *et al.*).⁸

The exposed surfaces of the test specimens were wet-ground up to 1200 silicon carbide (SiC) grit paper to produce a flush, clean surface. A thermocouple probe was placed laterally from 10 mm diameter specimens in specific experiments, touching its exposed surface for surface temperature (T_s) measurements; these specimens were not used for mass loss measurement due to the potential occurrence of galvanic effects. A laboratory scale TLC rig was developed,^{8,9} with the schematic drawing provided in Figure 2. The setup consists of a 2L glass cell with a specific lid integrated with an internal channeled matrix and test specimen slots, allowing flow of refrigerant to cool the surface of the TLC specimens to specific temperatures. The test specimen slot on the channeled lid allows the simulation of 12 o'clock position of a 6 inch diameter pipeline.

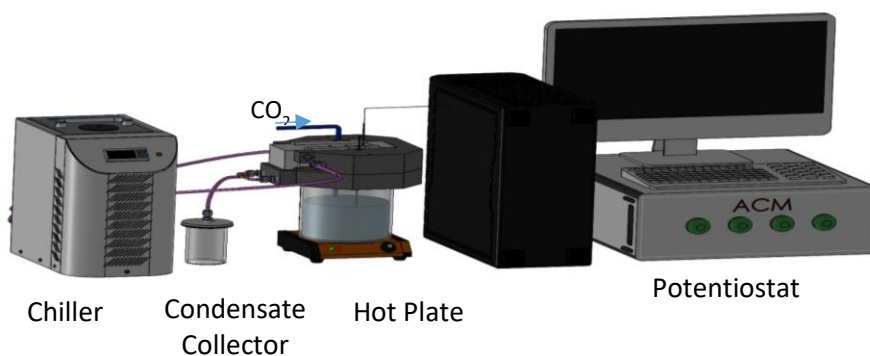


Figure 2: Top of line corrosion setup schematic diagram of the entire TLC experimental setup (modified from Folea *et al.*).⁸

The desired gas temperature (T_g) and surface temperature (T_s) were achieved by controlling the bulk fluid temperature in the 2L glass beaker using the hot plate. The refrigerant temperature (T_{ext}) in the channeled matrix was controlled using a chiller system. The test methodology and accuracy of temperature control for this specific rig can be found in previous work.^{8,9}

The bulk test solution consisted of CO₂-saturated 3.5 wt.% NaCl solution with two different concentrations of HAc (0 ppm and 1000 ppm), which was purged with CO₂ for a minimum of 12 h prior to each

experiment, to minimize the dissolved oxygen content. CO₂ was continuously bubbled into the cell throughout the test to avoid oxygen ingress. Colorimetric tests of dissolved oxygen were performed after each test to validate the saturation of the system and showed readings of less than 50 ppb.

The volume of condensed water in the graded collector was recorded and the water condensation rate (*WCR*) was calculated using Equation (1):

$$WCR = V_w / (L_s \cdot t_c) \quad (1)$$

where *WCR* is the water condensation rate in mL/m²s, *V_w* the volume of condensed water in mL, *t_c* is the duration time over which the condensed liquid is collected in s, and *L_s* is the internal area of the lid surface exposed to the vapor condensation (m²).^{8,9}

The condensate collector was also deaerated by bubbling continuously with CO₂ during the experiment to maintain the same environmental conditions. The pH of both bulk and condensate solutions (at their respective temperatures) were measured at the beginning and at the end of each test using an automatic temperature correction pH probe.

Additionally, condensate samples from all four different *WCR*s were collected to perform ionic chromatography analysis in order to quantify the amount of HAc that evaporated from the bulk solution and reached the top of line section.

Electrochemical measurements were performed using the miniature electrodes using a computer controlled potentiostat. Three electrochemical techniques were implemented in total. Linear polarization resistance (LPR) and electrochemical impedance spectroscopy (EIS), and Tafel polarization curves were employed to determine the *in situ* corrosion rate of the X65 carbon steel specimen. LPR measurements were performed by polarizing the sample ±15 mV vs the open circuit potential (OCP) at a scan rate of 0.25 mV/s to obtain a polarization resistance (*R_p*) and were undertaken every 20 minutes. The solution resistance (*R_s*) was measured over the course of the experiment using EIS. These measurements were performed using an amplitude of ±5 mV vs the OCP and the frequency range from 20 kHz to 0.1 Hz.

The value of *R_p* was corrected for *R_s* (Ω.cm²) in order to obtain the charge-transfer resistance (*R_{ct}*) value, and ultimately used to determine the corrosion rate with time using the Stern-Geary relationship in conjunction with Faraday's Law. For tests performed in the 4 different *WCR*s the average of *R_s* values were 5.6 ± 0.9 Ω.cm² in solutions without HAc and 4.3 ± 0.6 Ω.cm² in the presence of HAc.

Due to the droplet cycle process, there were some instances in which the electrochemical measurements were interrupted, resulting in noisy or erratic LPR responses. This phenomenon is associated with the intermittency of droplet contact between all three of the electrode probes. Under such instances, two scenarios can be hypothesized to explain such observations:

1. The droplet is no longer in contact with the carbon steel electrode, and corrosion ceases prior to the formation and/or growth of a droplet.
2. A droplet does exist at the carbon steel electrode surface, resulting in continued corrosion of the steel sample. However, electrochemical measurements are prohibited due to a lack of a consistent contact between the droplet and all three electrodes.

Each of the two aforementioned scenarios results in a different interpretation of the magnitude of corrosion rate during these intermittent periods, and it is likely that both scenarios occur during the experiment. However, the proportion to which each occurs is not clear. In order to produce conservative predictions of corrosion rates from the micro-electrodes in instances where electrochemical measurements were not possible, the corrosion rate was determined via interpolation between the nearest measurements in time either side of the erratic reading. (This is as opposed to assuming a corrosion rate of zero at such points.) To highlight the significance of processing such measurements in

this manner, it was determined that setting all ‘unreliable’ values to 0 mm/year resulted in a reduction of the corrosion rate by approximately ~10-15% in the most extreme cases, compared to the interpolation method. This result in smaller than the error associated with repeat measurements of the experiment.

After completion of each 20 h experiment, Tafel polarization curves were collected by performing individual anodic and cathodic sweeps, starting from OCP and scanning to -250 mV vs. OCP, for the cathodic branch, and to 150 mV vs. OCP, for the anodic branch, at a scan rate of 0.5 mV/s. From the polarization curves produced, it was possible to determine the anodic (β_a) and cathodic (β_c) Tafel constants in mV by measuring their respective gradient over regions where linearity was observed (on an E vs log(i) plot) and then determine the Stern-Geary coefficient (B), and ultimately the corrosion current density (i_{corr}) (Equation 2) which was converted into a rate of thickness loss in mm/year (Equation 3).

$$i_{corr} = \frac{B}{R_{ct}} = \frac{1}{R_{ct}} \frac{\beta_a \beta_c}{2.303(\beta_a + \beta_c)} \quad (2)$$

where B is the Stern-Geary coefficient, β_a is the magnitude of the anodic Tafel constant, and β_c is the magnitude of the cathodic Tafel constant (determined in separate experiments). The value of i_{corr} was then used in conjunction with Faraday’s Law and an appropriate conversion factor to obtain the corrosion rate in mm/year, as shown in the Equation (3), which was converted into a rate of thickness loss in mm/year, in accordance to ASTM G102.¹⁰

$$CR = K \frac{i_{corr} M_{Fe}}{nF\rho} \quad (3)$$

where K is a conversion factor to obtain corrosion rate (CR) in units of mm/year ($K = 3.16 \times 10^8$), i_{corr} is the corrosion current density in A/cm², M_{Fe} is the molar mass of iron (55.8g), n is the number of electrons freed in the corrosion reaction (2 electrons – Fe²⁺) and ρ is the density of steel (7.87g/cm³).

From analysis of the corrosion rate (CR) vs time curves produced from the electrochemical measurements, an average corrosion rate (ACR) was determined over the duration of each 20 h experiment, making it possible to compare the results obtained with the mass loss experiments performed in this study, as well as the work of other researchers.

Four different experimental conditions were generated by setting various combinations of T_g and T_{ext} in accordance with values reported in the literature.^{11,12} The experimental matrix of tests performed in this study are presented in Table 1. In summary, experiments were performed at two WCR values below the 0.25 ml/m².s ‘threshold’ and two above this value, with the latter two values simulating more severe conditions analogous to a system whereby external insulation may have failed in the field. Each of the four experimental conditions were studied in both the absence and presence of 1000 ppm HAC.

Table 1: Top of line corrosion tests matrix evaluated in this study

Bottom of the line solution	Temperatures				WCR (ml/m ² .s)
	T_{bulk} (°C)	T_{gas} (°C)	T_{ext} (°C)	T_s (°C)	
3.5% NaCl;	80	70	-10	42.5 ± 1.0	0.81±0.03
	80	70	30	50.3 ± 1.0	0.5±0.03
3.5% NaCl + 1000ppm HAC;	50	40	-10	20.5 ± 1.0	0.2±0.05
	50	40	30	32.5 ± 0.5	0.07±0.02

In order to understand the role of HAC in TLC, different surface analysis methods were implemented to complement the corrosion rate data extracted from mass loss and electrochemical measurement. Scanning electron microscopy (SEM) analysis was performed using a HITACHI Tabletop Microscope