A Study of Acetic Acid Role in CO_2 Corrosion

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1. Abstract

CO_2 corrosion caused by carbonic acid that formed when CO_2 gas dissolved in the water or brine that accompanies oil production at high pressures common in underground oil and gas reservoirs. Usually, CO_2 corrosion problems are manageable and under control. However, when small amount of organic acid that dominated by acetic acid is present in the system, the corrosion rate changes drastically. In this project, Electrochemical Impedance Spectroscopy (EIS) and Linear Polarization Resistance (LPR) was the measurement technique that being used in the project. EIS is a technique employed to study the mechanisme of CO_2 corrosion in presence of acetic acid, while LPR is a technique to determine the corrosion rate. All experiments were conducted in a 3% NaCl solution of pH 5.5 and temperature 60˚C.Based from results that was gathered from the experiment, LPR shows that corrosion rate for 1000ppm and 2000ppm of acetic acid increased significantly compared to blank CO_2. Meanwhile for 4000ppm, the corrosion rate decreased. This phenomenon was due to excessive non ionized acetic acid HAc. The carbonate ions from the iron carbonate could not dissolve the excessive amount of acetate leaving the iron ions to reacts with it and form iron acetate. Formation of $FeCO_3$ that decrease the corrosion rate can be proven from the trend of the data collection that shows significant decrease with time. It is correct to claim that in presence of acetic acid, the corrosion rate could increase significantly.

2. Introduction

Project Background - Carbon dioxide systems are one of the most common environments in the oil field industry where corrosion occurs. Areas where CO_2 corrosion is most common include flowing wells, gas condensate wells, areas where water condenses, tanks filled with CO_2, saturated produced water and flowlines, which are generally corroded at a slower rate because of lower temperatures and pressures. The material of construction for pipelines in the oil and gas industry is carbon steel for majority of facilities in production installations, because of its economical price, strength, and availability. However, carbon steel has a tendency to corrode in the presence of CO_2 and HAc.

Organic acid though weak, are known to affect the rate of CO_2 corrosion to a very large amount. The quantity of organic acids in produced water in the oil and gas system is in the range of 500 to 3000 ppm of which acetic acid contributes 50 percent to 90 percent of the organic acid. Classifications of organic acid can be done on the basis of molecular weight, and it was found that the lower molecular weight organic acids such as acetic acid were primarily soluble in water and can lead to corrosion of mild steel pipelines.

Problem Statement - CO_2 corrosion in oil and gas industries is often influenced by acetic acid or HAc. Weak organic acids such as acetic acid can commonly be found in oilfield brine. The presence of organic acid such as acetic acid or HAc has been considered as the main cause of mild steel pipeline failures. In oilfield pipelines, such as in CO_2 plant the corrosion issues are usually under control and manageable. However, when small amount of organic acid that usually dominated by acetic acid, the corrosivity of the pipeline can change dramatically. Therefore it is imperative to understand the role of acetic acid in CO_2 corrosion to apply appropriate and suitable corrosion prevention in order to preserve the equipments and pipelines.

Objective - The objective of this study is to understand the role and effect of different level of concentrations of acetic acid, HAc on CO_2 corrosion.

3. Literature Review

CO_2 Corrosion The corrosion mechanisms of CO2 and its effects on mild steel under varying conditions of pressure, temperature, pH, and oil-water fractioning has been a widely researched topic.[1] CO2 corrosion is a complex process as it is not only affected by the presence of multi corrosive species but also by other operational parameters such as flow, pH and material characteristic. The combined effect of these environmental and operational factors produce more aggressive environment which could result in increasing corrosion rate.[2]

Omkar (2004)[3] stated that one of the earliest efforts to explain the mechanism of CO_2 corrosion was explained by de Waard and Milliams (1975). More recent studies (1995, 2001,2003) have proposed models to predict CO_2 corrosion of mild steels based on their independent body of work. The key process of CO_2 corrosion will be shown below.

Carbon dioxide gas dissolves in water and forms a “weak” carbonic acid through hydration by water:

$$CO_2(g) \Leftrightarrow CO_2 \qquad (1)$$

$$CO_2 + H_2O \Leftrightarrow H_2CO_3 \qquad (2)$$

The carbonic acid (H_2CO_3) then partially dissociates to form the bicarbonate ion, which can further dissociate to yield the carbonate ion:

$$H_2CO_3 \Leftrightarrow H^+ + HCO_3^- \qquad (3)$$

$$HCO_3^- \Leftrightarrow H^+ + CO_3^{2-} \qquad (4)$$

De Waard and Milliams explained that the rate determining step for carbonic acid dissociation is the direct reduction of carbonic acid (H_2CO_3) and the corrosion rate is governed by the amount of undissociated acid in solution.[1,3] However, there are two possible cathodic reactions that can occur in the process of mild steel CO_2 corrosion: the above-mentioned direct reduction of H_2CO_3 but also reduction of hydrogen ions:[1]

$$H_2CO_3 + e^- \Rightarrow H + HCO_3^- \qquad (5)$$

$$H^+ + e^- \Rightarrow H \qquad (6)$$

The corresponding iron dissolution reaction is

$$Fe \Leftrightarrow Fe^{2+} + 2e^- \qquad (7)$$

The insoluble corrosion product of reactions 3, 4, and 7 is iron carbonate which forms by the reaction

$$Fe^{2+} + CO_3^{2-} \Leftrightarrow FeCO_3\,(s) \qquad (8)$$

When steel corrodes in CO2-saturated water, the solubility of iron carbonate salt (FeCO3) may be exceeded and precipitation sets in, which increases rapidly with the degree of supersaturation and an increase in temperature. The iron carbonate precipitatemay form a protective film depending on the solution composition, pressure, and temperature of the system. Other solid corrosion products may form in the presence of chlorides, sulfides, oxygen, etc. [1]

Acetic Acid Corrosion - The influence of HAc on the rate of corrosion of mild steel in oilfield brines containing CO_2 is well documented in literature and has been the subject of numerous studies since the 1980's[1].

Omkar (2004)[1] in his studies also stated that as early as 1983, Crolet and Bonis reported that the presence of acetic acid in the brine could increase the corrosion rate of carbon steel significantly. They also make the point that CO_2 induced acidification can cause partial reassociation of anions, such as acetates and propionates, to form organic acids. Such weak acids then will increase the oxidizing power of H^+ by raising the limiting diffusion current for cathodic reduction[5]. The presence of such acids also will tend to solubilize the dissolving iron ions suppress $FeCO_3$, or oxide film formation, which can otherwise passivate the steel surface[5].

Omkar (2004)[1] said that Hedges and McVeigh (1999) [1] later confirmed this but the interconversion of HAc and Ac^- ions as given by equation (9) was not accounted for. In the presence of Ac^- ions, the corrosion rate can increase even if the pH increases leading to errors in prediction models for corrosion rates. The presence of both HCO_3^- and Ac^- cause erroneous titration results leading to an overestimation of pH.

The presence of acetate (Ac^-) is the result of which comes from the dissociation of HAc

$$HAc \rightleftharpoons H^+ + Ac^- \qquad (9)$$

leads to an overestimation of pH when the HCO_3^- analysis is carried out leading to significant under prediction of corrosion rates. The equilibrium constant for equation (9) is K_{HAc} and expressed as

$$K_{HAc} = \frac{[H^+][Ac^-]}{[HAc]} \qquad (10)$$

K_{HAc} is dependent on temperature (Tc, Celcius) and was first expressed by Kharaka (1989)[1]

$$K_{HAc} = 10^{-(6.66104 - 0.0134916 * (273 + Tc) + 2.37856*10\text{^}-5 * (273 + Tc)\text{^}2)} \qquad (11)$$

In equation (10) the total amount of HAc, [HAc] and the temperature are known. So, K_{HAc} is also known. Thus the concentration of H^+ ions, $[H^+]$ or the pH value determines how much of the acetic acid will dissociate. Thus different pH values represent different amounts of undissociated (free) HAc which is the main cause of concern as it was found to increase the corrosion rate. HAc acts as a reservoir of H^+ ions, which readily accept electrons produced by the iron dissolution reaction.

George (2003)[14] suggested that HAc does not affect the charge transfer mechanism of the cathodic reaction but only affects the limiting currents.

Omkar (2004)[1] stated that Sidorin (2003) did voltammetry experiments on steel rotating disc electrode (RDE) and found that solutions containing Ca^{2+} and Fe^{2+} ions do not change the equilibrium concentration of HAc significantly although they increase the ionic strength of the solution.

Crolet et al. (1999)[12] showed that for uniform corrosion beneath a protective layer the free HAc is exhausted and in such a situation the acetic buffer was decisive in determining the protectiveness of corrosion products. He also reported an inhibtion of the anodic dissolution reaction of iron in presence of Ac^- ions.

Garsany et al. (2002,2003)[15] in their work used cyclic voltammetry to study the effect of Ac^- ions on the rates of corrosion using a rotating disc electrode (RDE) in the absence of film formation. They emphasized that the electrochemistry of acetic acid at steel cannot be distinguishable from that of free proton (because of its rapid dissociation) and predicted that the increased rate of corrosionis proportional to the concentration of undissociated acetic acid in the brine.

Joosten et al. (2002)[13] examined acetic acid, synthetic seawater and an oil phase in glass cells and found that HAc increased the corrosion rate by decreasing the pH. He also found evidence of localized 13% Cr steel at 95˚C and 600 ppm HAc.

George (2003)[14] investigated the effects of HAc on the cathodic and anodic reactions of CO_2 corrosion using Linear Polaarization Resistance (LPR), Electrochemical Impedance Spectroscopy (EIS), and potentiodynamics sweeps. He concluded that HAc did not affect the charge transfer mechanism of the cathodic reaction but did affect the limiting currents. At room temperature (22˚C) the HAc acts as a source of hydrogen ions and HAc needs an “activation time” for its effect to be measured.

Mehdi (2010)[6] mentioned that, based on the study from Nafday and Nesic, HAc cannot cause any localized corrosion, has no effect on the thickness of corrosion product iron carbonate ($FeCO_3$) layer but affects layer morphology. However, Okafor and Nesic reported that acetic acid can caused localized corrosion by removing iron carbonate layer. He also stated that George and Nesic reported that the presence of HAc strongly affects the cathodic limiting current. The anodic reaction (iron dissolution) was unaffected or mildly retarted with increasing HAc concentration at room temperature.

Liu et al.(2008)[16] investigated the effect of HAc using electrochemical impedance spectroscopy (EIS). They found that the surface chemical reactions of cathodic reduction were enhanced in the presence of HAc. They also found that HAc can remove $FeCO_3$ layer. Zhang and Cheng[8] reported similar results. In addition, they observed an increase in the current density of anodic reactions and they saw localized corrosion on the surface of steel.

Iron Carbonate ($FeCO_3$) Film Formation - Iron carbonate ($FeCO_3$) film formation is the main corrosion product in the CO_2 corrosion process. Film formation is strongly dependent on the thermodynamics and kinetics of $FeCO_3$ precipitation. Supersaturation plays the most important role in $FeCO_3$ film growth and its morphology. A high supersaturation of $FeCO_3$ is necessary to form a protective film, particularly at low temperatures[5]. In principle, the precipitation process comprises two steps, nucleation and particle growth. The morphology of the film therefore depends on the dominating step[5]. The reaction for formation of solid iron carbonate is given by:

$$Fe^{2+} + CO_3^{2-} \rightleftharpoons FeCO_3(s) \qquad (12)$$

$FeCO_3$ forms on the wall of the pipe if the product of ferrous ion concentration (Fe^{2+}) and carbonate ion concentration (CO_3^{2-}) exceeds the solubility product limit[1]. A measure of when the film is likely to precipitate is supersaturation value (SS) defined as

$$SS = \frac{[Fe^{2+}][CO_3{}^{2-}]}{[Ksp_{FeCO_3}]} \qquad (13)$$

The film will precipitate when the SS value exceeds unity. However, the rate of precipitation of iron carbonate can be so slow that often the precipitation kinetics becomes more important than the thermodynamics of the process. The equilibrium constant for iron carbonate film Ksp_{FeCO3} is dependent on temperature (Tc, Celcius) and ionic strength (I) and expressed as

$$Ksp_{FeCO3} = 10^{(-10.13 - 0.0182*Tc)} / (0.0115 * I^{0.6063}) \qquad (14)$$

$$I = 0.5 * \Sigma nZ^2 \qquad (15)$$

where I represents the number of ions, Z is charge of each ion and n is the molar concentration of each ion[1].

$FeCO_3$ reduces the corrosion rate by reducing and virtually sealing film porosity[5]. It is also believed that increasing the temperature would improve the protectiveness of the $FeCO_3$ scale as well as its adhesion and hardness and that the higher the temperature, the more improved the protectiveness[5]. However, there is a little agreement on a practical “threshold” temperature. Some have reported that the maximum corrosion rate observed for carbon steel in sweet environments was from 60˚C to 70˚C and then it started to decline due to growth of protective $FeCO_3$ films[5]. In another studies[5], it has been suggested that the lowest temperature necessary to obtain $FeCO_3$ films that would reduce the corrosion rate significantly was 50˚C and the protectivenes was increased also by increasing the pH.

From a study, Omkar (2004)[1] mentioned that Johnson and Tomson (1991) used a "temperature ramped" approach to calculate the activation energy of $FeCO_3$ precipitation and found that precipitation was controlled by the surface reaction rate. The most important factors which affect the precipitation of iron carbonate film are supersaturation and temperature. The film is known to be protective and corrosion rate drops once the film starts growing. When $FeCO_3$ protective film forms, its growth is very temperature sensitive. Its composition, structure and thickness and physical properties are determined by the film precipitation mechanisms. A frequently used expression for the rate of precipitation of iron carbonate ($R_{FeCO3(s)}$) is given by Van Hunnik et al. (1996) as stated by Omkar (2004)[1]

$$R_{FeCO_{3(s)}} = \frac{A}{V} .f(T).K_{sp}.f(SS) \qquad (16)$$

where A is the surface area of the electrode and V is the solution volume.

When iron carbonate precipirares at the steel surface, it decreases the corrosion rate by presenting a diffusion barrier for the species involved in the corrosion process and blocking a portion of the steel and preventing electrochemical reactions from occuring.

4. Methodology

30g of NaCl was weighed and dissolved in 1000ml deionized water to produce 3 percent NaCl solution. The solution of 3% percent NaCl was poured into a glass cell where the experiment will be done.

The NaCl solution was then bubbled with CO_2 for 1 hour prior to the exposure of the electrode and maintained throughout the experiment. The purpose of the CO_2 purging is to ensure that all the oxygen is removed from the water and to maintain the saturation of CO_2. The required test temperature is also maintained throughout the experiment using a hot plate. The electrochemical measurements are based on a three-electrode system, using a commercially available potentiostat with a computer control system. The reference electrode used is an Ag/AgCl and the auxiliary electrode is a platinum electrode.

The working electrode is prepared from X52 pipeline steel (elemental composition is shown in Table 3). The sample was spot-welded with nickel-chromium wire and mounted in araldite resin with an exposed area of 0.1 cm^2. The sample surface is then polished to 600-grade finish using silicon carbide papers. The specimen is degreased and rinsed with ethanol and deionised water before immersion.

The sample is then immersed in the 1 liter of 3% NaCl solution which has been prepared earlier and purged with CO_2 for about 45 minutes while being heated up until the temperature reached the desired value. Then, the pH is measured and 1M of sodium bicarbonate solution is added into the solution until the pH becomes 5.5. The experiment is then ran for 0 ppm of HAc for 24 hours and the data of the LPR and EIS is collected.

The experiment is repeated for different concentrations of HAc injected as stated in the test matrix. The data collected will then be analysed.

Linear Polarization Resistance - This method is based on the linear approximation of the polarization behavior at potentials near the corrosion potential. Polarization resistance (Rp) is given by Stern-Geary equation:

$$Rp = \frac{B}{i_{corr}} = \frac{\Delta E}{\Delta I} \qquad (26)$$

Where, $B = \frac{b_a b_c}{2.303(b_a+b_c)}$ (27)

The value of B used is 26 mV/decade. The corrosion current can be related directly to the corrosion rate from Faraday's law:

$$CR\ (mm/year) = \frac{315Zi_{corr}}{\rho nF} \qquad (28)$$

Where,

CR = corrosion rate, mm/year
i_{corr} = corrosion current density, $\mu A/cm^2$
ρ = density of iron, 7.8 g/cm^3
F = Faraday's constant, 96500 C/mole
Z = atomic weight, g/mol
n = electron number
b_a,b_c = the slopes of the logarithmic local anodic and cathodic polarization curves respectively
Rp = resistance polarization, ohm

Linear polarization resistance measurements were performed by firstly measuring the corrosion potential of the exposed sample and subsequently sweeping from -10mV to +10mV with the sweep rate of 10mV/min.

Electrochemical Impedance Spectroscopy - The EIS set up consists of an electrochemical cell (the system under investigation), a potentiostat, and a frequency response analyser (FRA). The FRA applies the sine wave and analyses the response of the system to determine the impedance of the system.

The electrochemical cell in an impedance experiment can consist of two, three, or four electrodes. The most basic form of the cell has two electrodes. Usually the electrode under investigation is called the working electrode, and the electrode necessary to close the electrical circuit is called the counter electrode. The electrodes are usually immerses in a liquid electrolyte. For solid-state systems, there may a solid electrolyte or no electrolyte. In this experiment, three electrodes systems are used which are the working electrode, the reference electrode, and the auxilliary electrode.

For the potentiostat, experiments were done at a fixed DC potential. A sinusoidal potential perturbation is superimposed on the DC potential and applied to the cell. The resulting current is measured to determine the impedance of the system. The experimental setup for the project is shown in Figure 3.

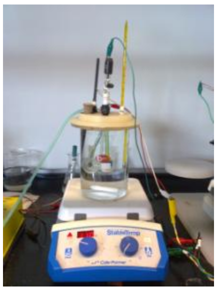

Figure 3: An image for the test set up

5. Results and Discussion

Linear Polarization Resistance (LPR) - The average corrosion rates of X52 carbon steel exposed to concentrations of HAc from 0 to 4000 ppm at pH 5.5 and temperature 60˚C are summarized in the Figure 4.

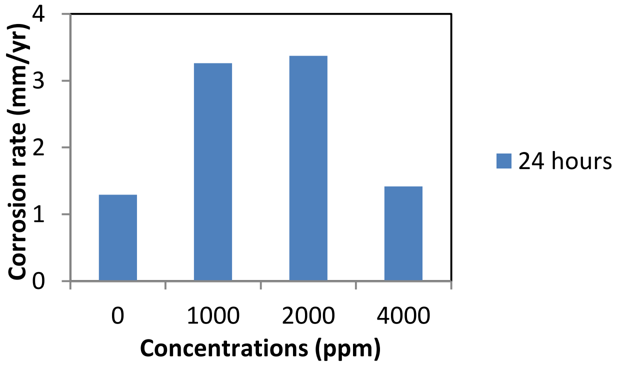

Figure 4: Graph of corrosion rate vs acetic acid concentrations

From Figure 4, it is observed that the average corrosion rate in the absence of acetic acid was about 1.0 mm/yr and was rather low as iron carbonate layer formed.

The corrosion rate increases significantly for concentration of 1000ppm and 2000ppm compare to 0ppm. This contributes to a lower Fe^{2+} supersaturation in the corrosion film and at the steel surface. The presence of acetate ions (Ac$^-$) in acetic acid also is prone to solubilize the dissolving iron of ions (Fe^{2+}) and suppress iron carbonate layer which can deactivate the steel surface. The reaction of Fe^{2+} and Ac$^-$ occurs at a high rate and forms iron(II) acetate (FeAc) which is highly soluble in water.

On the other hand, the iron carbonate (FeCO$_3$) that was formed from Fe^{2+} and CO$_3^{2-}$ occurs at a very slow rate as compared to that of FeAc. Therefore, more Fe^{2+} ions will react with Ac$^-$. As the concentration of acetic acid increase, the solubility of iron acetate is also increased even the pH is maintained.. Thus, the rate of corrosion increased as the exposed area of the carbon steel increase when the solubiliity of iron acetate increased.

However, the corrosion rate decreased significantly with the addition of 4000 ppm of acetic acid. The corrosion rate dropped to values which was even lower than that of the blank solution (0 ppm). This happens due to the excessive amount of acetic acid concentration in which the iron carbonate failed to dissolve. In an excessive amount of acetic acid, there might be possibility that FeAc formed much more than its solubility. As a result, FeAc will form another layer of film on the steel surface thus preventing the corrosion from happening.

Electrochemical Impedance Spectroscopy (EIS) - The Nyquist plots obtained for the sample at different concentration of HAc injected at pH 5.5 and temperature 60˚C after 2 hours are shown in Figure 5.

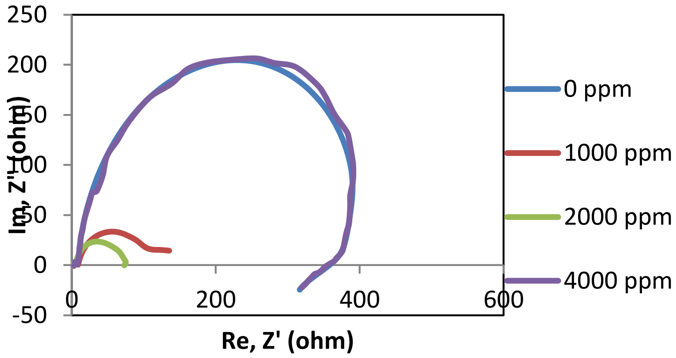

Figure 5: Nyquist plot of the effect of HAc at four different concentrations

Figure 17 shows a very large capacitive loop in the blank solution (0 ppm) and could be considered as the capacitance of double electrode layer between the corrosion scale and solution. This is followed by another capacitive loop for other concentrations of acetic acid.

It is known that iron carbonate film or layer will form and act as a protective scale on the surface of the steel surface if the reaction is given long and enough time to react, preventing the corrosion from happening. When the layer is completely compact, the corrosion is controlled by a diffusion process. However, if there are some pores in the layer, a charge transfer process at the layer/steel interface occurs. This will change the corrosion mechanism to the charge transfer and the shape of impedance plot at low frequencies to a capacitive loop.

At 1000 ppm of acetic acid, the capacitive loop at diminished significantly and the loop became smaller. It could be seen from the plots that there was a drastic decrease of the impedance values in the presence of 1000 ppm of acetic acid. The shrinkage of the loops shows an increase in corrosion rate and therefore a decrease in the protectiveness of iron carbonate layer. Therefore, active species, such as FeAc, could get to the steel surface easier resulting in an increase of the corrosion rate.

When the concentration of acetic acid is increased to 2000 ppm, the capacitive loop became much smaller than the previous condition as the impedance is diminished. As stated earlier, the shrinkage of the loop means even much less protective iron carbonate layer and an increase in the corrosion rate.

On the other hand, in the presence of 4000 ppm of acetic acid, the capacitive loop expanded and the values of the impedance became bigger. This results from an excessive amount of concentration of undissociated acetic acid injected into the solution. The excessive Ac^- ions from the acid reacts with the Fe^{2+} ions from the steel as the rate of reaction of these ions are much higher than that of $FeCO_3$. This reaction, which forms in a much higher rate than it solubility, will form iron acetate (FeAc) which will act as another protective layer on the steel surface, thus, reducing the corrosion rate.

6. Conclusion & Recommendations

Based on the results obtained, the corrosion rate increased with the addition of 1000 ppm and 2000 ppm of acetic acid. However, with the addition of 4000 ppm of acetic acid, the corrosion rate decreased.

In the presence of 1000 ppm of acetic acid, the corrosion rate started to increase as the acetate ions from the acid tends to solubilize the dissolving iron ions and suppress iron carbonate layer which can passivate the steel surface. The solubility of iron acetate increases as the concentration of acetic acid increases. Thus, the presence of 2000 ppm of acetic acid will expose the surface of the steel even more and increase the corrosion rate.

On the other hand, in the presence of 4000 ppm of acetic acid, the corrosion rate decreased significantly and is believed due to the excessive amount of concentration of acetate ions in the solution. The carbonate ions from the iron carbonate could not dissolve the excessive amount of acetate leaving the iron ions to reacts with it and form iron acetate. However, it is still not clear how the iron acetate compound will affect the steel surface.

It is recommended that the energy dispersive x-ray (EDX) analysis also should be done in order to confirm the presence of any compound on the steel surface.

7. References

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