

The Effect of Acetate Ions on CO₂ Corrosion of Mild Steel at Different pHs

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Abstract :

carbon dioxide corrosion is the main source of failure in most of the oilfields. Interactions between some species, such as acetate or acetic acid, and operating conditions such as pH and temperature, could influence the CO₂ corrosion mechanism. For static condition, this work studies, the effect of acetate ions containing solution with variation of pH on mechanism and behaviours of CO₂ corrosion rate , typically of oilfield waters. However, the experiments were carried out on mild steel immersed in brine environment of 3% NaCl at room temperature, free of oxygen and saturated with carbon dioxide or nitrogen. The electrochemical studies were based on linear polarization resistance (LPR). Based on the LPR

results, the corrosion rate is significantly influenced by the presence of acetate specially at low pH for both systems 'N₂ and CO₂', except at high concentration, which could be due to inhibition by acetate or acetic acid. However, the maximum corrosion rate is obtained was at 600 ppm acetate and pH 3.8; the corrosion rate is raised almost 3 times when compared with value obtained in the CO₂ only at the same pH. Furthermore, the addition of the contribution of the corrosion impact from CO₂ only and acetate or acetic acid only ' with N₂' not represent the exact behaviour of the acetate saturated with CO₂, this perhaps due to some interaction between them to give higher corrosion rate.

Key words: CO₂ corrosion, concentration of acetate, pH, linear polarization resistance, static condition.

1. INTRODUCTION:

CO₂ corrosion is the most prevalent form of corrosion attack associated with the oil and gas industry. In hydrocarbon deposits for millions of years, the chemical species CO₂ has been in equilibrium between the three phases. The first reported genuine CO₂ corrosion related problem appeared in Texas in the 1940's, however before that the chemical industry had performed laboratory studies related to the effect of CO₂ on corrosion by measurements of pH and its effect on the corrosion rate [1] .

The corrosion rate of steel in carbon dioxide containing solution is a function of many variables including temperature pH, carbon dioxide partial pressure, flow rate, solution composition, metal composition and microstructure and corrosion product film formation. The combined effect of these factors produces an aggressive environment whereby the survival of carbon steel pipeline is not guaranteed.

Pipelines are mainly made of carbon steel due to many advantages such as availability, low cost, and ease of fabrication over other metals. Unfortunately, carbon steel has lower resistance to carbon dioxide corrosion. Thus, the challenge in carbon dioxide (CO₂) corrosion research is to understand the limitations of the use of carbon steel pipeline for the purpose of huge potential economic savings.

CO₂ corrosion in the presence of acetic acid (HAc) has been studied since 1983 and particularly in the late 1990s. Many papers related to CO₂ corrosion have been published and a large variety of corrosion rates and mechanisms have been reported. It is found that the presence of Acetate (AC⁻) in oilfield brines can significantly increase the rate of corrosion of carbon steel. In the presence of AC⁻, the corrosion rate can increase even if the pH increases. Many corrosion predication models cannot accommodate this observation [12]. On a ppm basis, AC⁻ increases the corrosion rate more than the HCO₃⁻ decrease it. The presence of AC⁻ only effects the corrosion rate and not the corrosion mechanism. The mechanism by which HAc increases the corrosion rate perhaps explained by its ability to both decrease the pH and solubilise Fe²⁺, thus reducing the iron carbonate film thickness [12].

Many experiment works were conducted to investigate the effect of the presence of HAc in CO₂ corrosion for both static and turbulent conditions [2–11]. Varied results were achieved on the effect of different HAc concentrations on the CO₂ corrosion rate.

Hedges and McVeigh (1999) used the rotating cylinder electrodes to study the effect of acetate in CO₂ corrosion. They concluded the increased corrosion rates were attributed to the formation of thinner iron carbonate films, since acetate ions have the ability to form iron acetate and transport

iron away from the steel surface. However, they didn't control the pH change in their experimental.

Pletcher et al., 2003 studied the role of acetate in CO₂ corrosion of carbon steel related to oilfield conditions. They used voltammetry on the X65 carbon steel electrodes

fabricated from rods, diameter 0.48 cm, to study the effect of acetate on carbon steel corrosion. they did many experiments with different conditions for example different temperatures and compared the results in Voltammograms.

Sun et al., 2003 investigated the effect of HAc on the part reactions under N₂ and CO₂ atmospheres at room temperature. Polarization curves showed that HAc increased the cathodic current, and that the H₂ evolution from HAc was activation controlled at room temperature. In fact, they didn't change the pH in their experimental. Ismail (2005) concluded that at an HAc concentration of more than 400 ppm illustrated an inhibitive property. However, a low HAc is of great concern as it also increases the corrosion rate .

Even though there are many extensive CO₂ corrosion studies, the mechanism of CO₂ corrosion in the presence of AC⁻ is still not clear. In this study, the corrosion behavior of mild steel in a CO₂ environment with different concentrations of acetate with variation of pH was investigated by electrochemical measurements under oilfield conditions. It is expected that this research will provide an essential insight into the corrosion of carbon steel with varies concentrations of AC⁻ in a CO₂ environment.

2. EXPERIMENTAL:

2.1. *Martial:*

The steel used was mild steel rod of 0.785 cm² surface area. All the reagents were of analytical grade. Water used throughout the experimental work was deionised of conductance. Working temperature and pressure were normal room temperature and atmospheric pressure. Carbon dioxide and nitrogen used for purging the working solution were of commercial grade. Experiments under static condition was conducted with mild steel with the composition shown in table 1.

Table 1 The Chemical Composition of Mild Steel (wt%)

C	Mn	P	S	Si	Cr	Ni	Mo	Cu	Fe
0.18%	0.81%	0.003%	0.029%	0.25%	0.08%	0.11%	0.0018%	0.26%	Balance

2.2. *Linear Polarization Resistance (LPR):*

The linear polarization method is a widely used method of measuring corrosion rate and is based on the equation, which was developed by Stern and Geary from earlier work by Wagner and Traud . This technique works by taking a linear section of the polarization curve near (± 10 mV) the corrosion potential of the metal and makes it possible to find the ratio existing between the ($\Delta E = E - E_{\text{corr}}$) and the applied current ΔI for polarization of typically less than 10 mV.

Therefore

$$R_p = \Delta E / \Delta I$$

Where

R_p = polarization resistance and the corrosion theory shows that for an activation controlled system.

$$I_{\text{corr}} = \beta / R_p$$

Where β is a constant for the metal / environment combination.

This is called the Stern – Geary relationship.

$$\Delta E / \Delta I = R_p = \frac{b_a \times b_c}{2.3 \times I_{\text{corr}} \times (b_a + b_c)}$$

Where

R_p is a polarization resistance

I_{corr} is the corrosion current

b_a and b_c are Tafel constants for anodic and cathodic processes.

Corrosion rate calculations were performed for each concentration. Corrosion rate was calculated according to the Stern-Geary equation, which was used to calculate corrosion rates (β is 25 mv) and then converted to mm/year using Faraday's law as shown in equation below:

$$\text{CR (mm/year)} = \frac{31.5 \times 10^7 Z_i I_{\text{corr}}}{\rho n F}$$

where

CR = Corrosion rate (mm/year)

I_{corr} = Corrosion current density, A/cm²

ρ = Density of iron, 7.8 g/cm³

F = Faraday's constant, 96500 C/mole

Z = Atomic weight, 56g/mol

n = number of exchanged electron.

2.3.Solutions Preparation:

3% NaCl solution was prepared by adding 30 grams of NaCl in one litre of distilled water for each test, which gives a pH =3.8 after the solution has been saturated by CO₂ gas. The pH of the solution can adjust by adding a calculated amount of 1M NaHCO₃ (sodium hydrogen carbonate) to the prepared solution.

To get pH =5.5 required 7 to 8 ml of 1M NaHCO₃ solution to be added to the prepared solution of pH =3.8. The pH value (± 0.1) was checked by pH-meter which had been previously calibrated by using buffer solutions.

Analytical grade powder sodium hydrogen carbonate was dissolved in one litre of deionised water to give one molar (1M) solution in order to adjust the pH of the working solution.

To enable use of various concentration of (HAc), (1M) concentrated (stock solution) was prepared by dissolving 60g of acetic acid in a litre of deionised water.

To enable use of various concentration of sodium acetate (NaAc) (1M) concentrated (stock solution) was prepared by dissolving 82 g of NaAc in a litre of deionised water. Acetate solutions of different pH were prepared by mixing the acetic acid with sodium acetate solutions in deferent preparations.

2.4.Sample Preparation:

All specimens used in this work were prepared from commercial mild steel cylindrical rod of (0.785 cm²) cross section area. To use mild steel rod as working electrode many steps were carried out to achieve a final useable electrode:

- a) The steel rod was cut into pieces of 1 cm length each using an electric saw.
- b) To achieve electrical contact of the specimen a length 25 cm nichrome wire was spot welded to it.
- c) The nichrome wire was fed through 5mm diameter plastic tube.
- d) For the purpose of polishing and ease of handling the steel specimen was mounted in Araldite.
- e) The dry mould was then ready for polishing, wet polishing was used all the time using silicon carbide cloths from coarse 240 grit through 320 ,400, 600 to a final value of 800.
- f) Specimens are then degreased using acetone , followed by washing with deionised water, drying in hot air and storing in a dry dessicator prior to exposure to the test solution. The time gap between the use of polished specimens and their use kept always as short as possible and did not exceed 30 minutes even in the worst cases.

The specimens were re-polished and degreased to be used for further tests for a maximum of 5 times to avoid the formation of any crevices between the steel and the Araldite mould which give rise to misleading higher corrosion rates.

2.5. Electrochemical Corrosion Test Cell:

A standard one litre electrochemical cell was used for this work . The electrochemical corrosion rate measurements in term of R_p were carried out in standard three-electrode electrode electrochemical cell as shown in figure1. The cell was designed in such a way that air can be prevented from entering into the solution by deaeration with continuous bubbling of carbon

dioxide or nitrogen. The standard electrochemical cell consists of platinum electrode was used as auxiliary electrode, working electrode (mild steel), and reference electrode (Ag/AgCl).

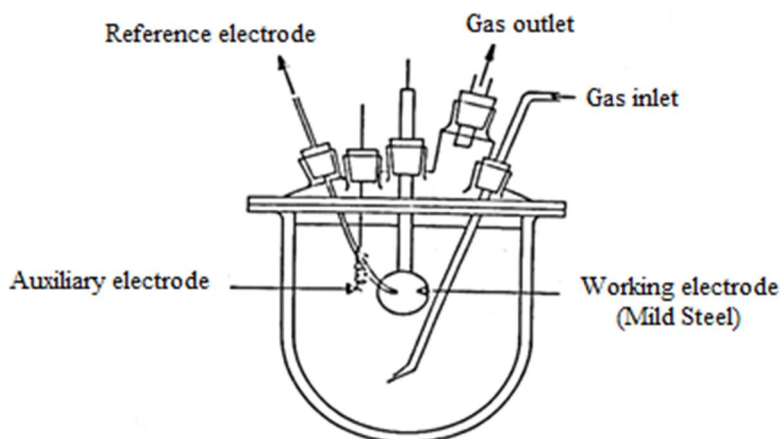


Figure 1 Electrochemical cell

2.6. Experimental Procedure:

All experiments were performed at ambient temperature. Before the specimen was immersed in the solution, the solution was de-aerated by passing CO₂ or N₂ for about two hours to ensure that no more oxygen gas was left in the solution. The pH values were always checked to make sure that the working solution was accurate. The reference electrode was always situated in potassium chloride solution to prevent the poisoning of the electrode itself by the added acetate.

After the solution was made, CO₂ or N₂ was bubbled for around two hours. The mild specimen was immersed in the solution containing 3% NaCl at different pH's 3.8, 4.8, 5.5 and 6. This test was done at different concentrations of acetate at the same pH, for example pH=3.8 mixed acetic

acid (1M) with sodium acetate(1M) at ratio (10:1), and pH =5.5 mixed acetic acid (1M) with sodium acetate(1M) at ratio (1:5). The main concentrations of acetate used were 60 ppm, 300 ppm, 600 ppm and 1200 ppm.

Polarization resistance measurements were performed using a ACM electrochemical unit model 332, controlled by a 486-DX2 personal computer with Auto-LPR software.

Duration of tests were run for minimum period of 12 hours for acetate solutions, and the same period of running time for blank (without acetate) solutions to investigate the effect of acetate on CO₂ corrosion.

2.7. Reproducibility of Results:

The acetate concentrations performances were usually checked many times. To confirm the result obtained are compatible with each other, which may effected by contamination or the position of the working electrode with respect to reference and auxiliary electrodes. Also, due to the rate of CO₂ or N₂ bubbling and change in room temperature. The reproducibility of the result was similar to that obtained before.

3. RESULTS AND DISCUSSION:

3.1. Influence of pHs:

Figures 2 to 5 showed the average corrosion rate (mm/year) for the whole range of pHs from 3.8 to 6 for solutions with CO₂ only, 60 ppm , 300 ppm , 600 ppm and 1200 ppm acetate, with nitrogen and the same acetate concentration . In figure 2 the concentration of acetate (60 ppm) is not very high and the effect is only slight at higher pHs. High corrosion

rate caused by acetate with CO₂ at pH 3.8 it is about 2.3 mm/year and decreases with increased pH at pH 6 it is about 1.6 mm/year. However, at pH 4.8 the corrosion rate caused by CO₂ only is about 1.1 mm/year, but the corrosion caused by 60 ppm acetate saturated with CO₂ is about 2mm/year, the 60 ppm acetate increases the corrosion rate about 2 times compared to the system saturated with CO₂ only.

It can be seen From Figure 3 that a very high corrosion rate, almost 2 times higher than the one obtained for system saturated with CO₂ only at pH 3.8. At the same time it was seen that the corrosion rate decreases with increased pH and the ratio of increasing corrosion rate decreases as well. At pH 6 it is about half times higher than that obtained for CO₂ only without acetate.

At the high concentration of acetate (600 ppm) used, it can be noticed from Figure 4 that when both the concentration of HCO₃⁻ and the pH solutions increased, the corrosion rate decreased. As the concentration of acetate increased the corrosion rate increased. For example at pH 3.8 the corrosion rate increases 3 times compared to that caused by CO₂ only. This perhaps explained by the fact that at this pH and high concentration of acetate or acetic acid more protons are available. The corrosion rate decreased with increased pH for acetate only with nitrogen and acetate saturated with CO₂. However, the presence of acetate in the solution increases the CO₂ corrosion of mild steel with increase. The observation also shows the corrosion rate caused by acetate only is close to the corrosion rate by CO₂ only at pH 3.8 and decreases with increased pH. This observation perhaps due to high concentration of acetic acid at pH 3.8.

It can be noticed from figure 5 that there is a large difference between the behaviour of 1200 ppm and the other concentrations.. At pH

3.8 and 4.8 it shows a decrease in corrosion rate at this concentration of acetate. This decrease in corrosion rate indicates that possibly there is some inhibition by acetate or acetic acid. This behaviour is not fully understood and needs further work for confirmation.

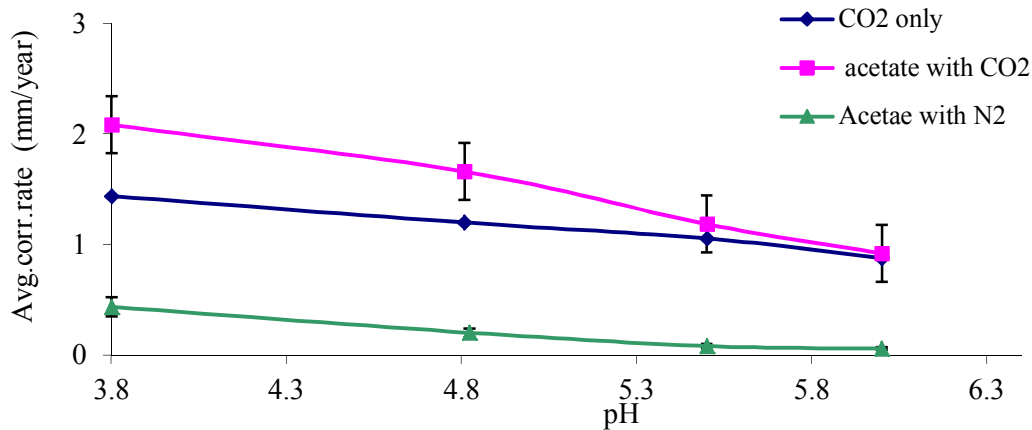


Figure 2 Average corrosion rate (mm/year) .vs. pHs at (60 ppm) acetate with CO₂ & N₂

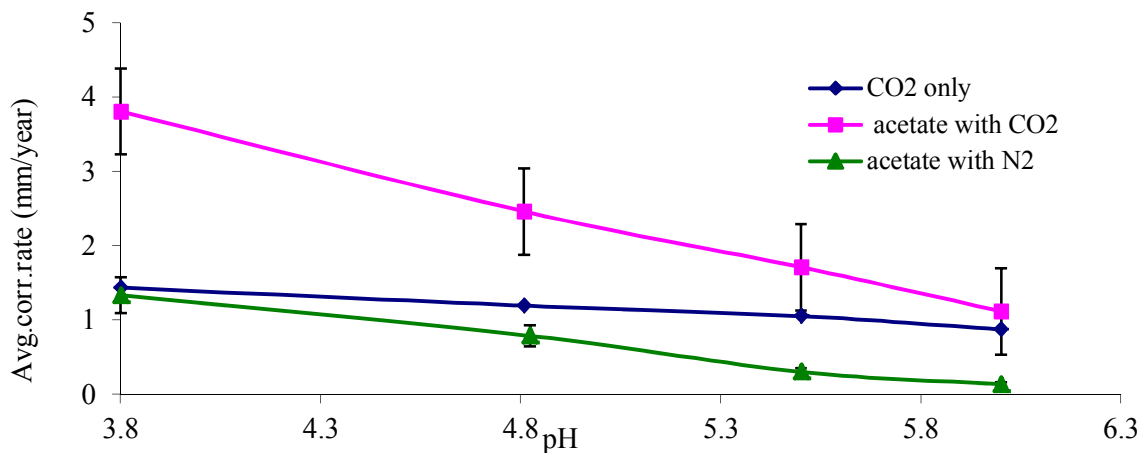


Figure 3 Average corrosion rate (mm/year).vs. pHs at (300 ppm) acetate with CO₂ & N₂

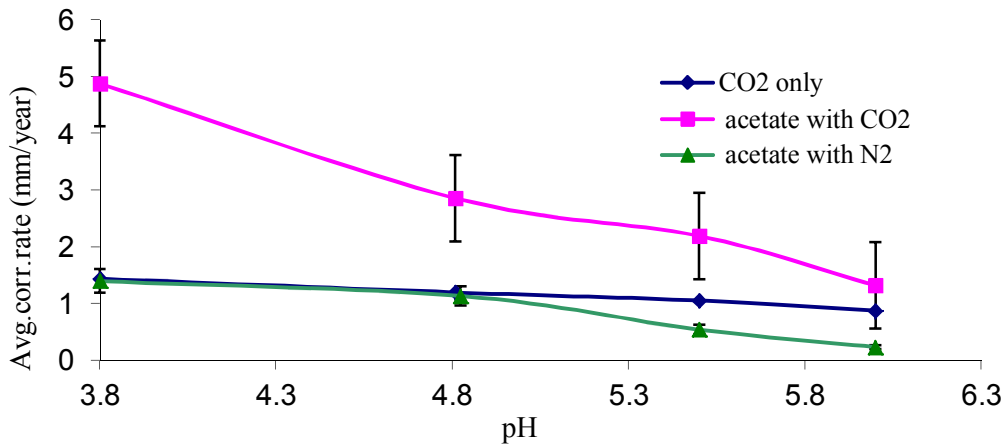


Figure 4 Average corrosion rate (mm/year) .vs. pHs at (600 ppm) acetate with CO₂ & N₂

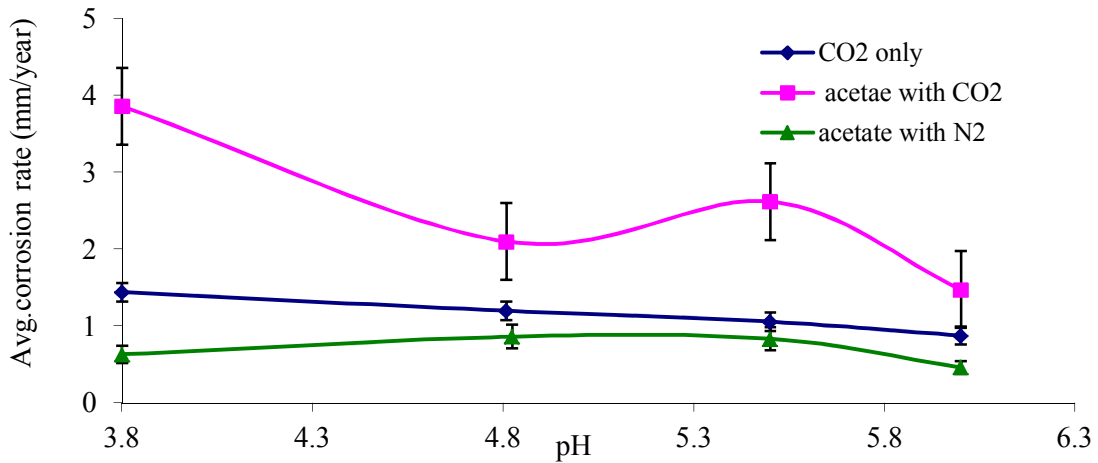


Figure 5 Average corrosion rate (mm/year).vs. pHs at (12000 ppm) acetate with CO₂ & N₂

3.1.1. Overall Effect Of Total Acetate AC On CO₂ Corrosion At Different pHs

Figure 6 shows that the highest corrosion rate observed when the solution have high concentration of acetate with CO₂ except at very high

concentration of acetate, the corrosion slightly decrease. Furthermore, the corrosion rate has maxima at 600ppm for both solutions of the pH 3.8 and the pH 4.8, and slightly decrease at 1200 ppm as shown in figure 6 below. However, the highest corrosion rate was obtained at pH 3.8 for the all concentrations and then pH 4.8. The mechanism by which acetate increases the corrosion rate perhaps explained by its ability to both decrease the pH and solubilise Fe²⁺, thus reducing the iron carbonate film thickness. Moreover, this increase of corrosion rate is due to in the absence of acetate a film of iron carbonate specially at high pHs is formed though which the H⁺ has to diffuse, but when AC⁻ ion is present some of the ion is transport away from the steel surface and the carbonate film is thinner when AC⁻ ion is present. Thus, even though the bulk pH of the solution is higher (less H⁺), the rate of transport of H⁺ to the steel surface is faster because it has less film to travel through i.e. the film thinning effect is more pronounced than the decrease in H⁺ concentration effect [12].

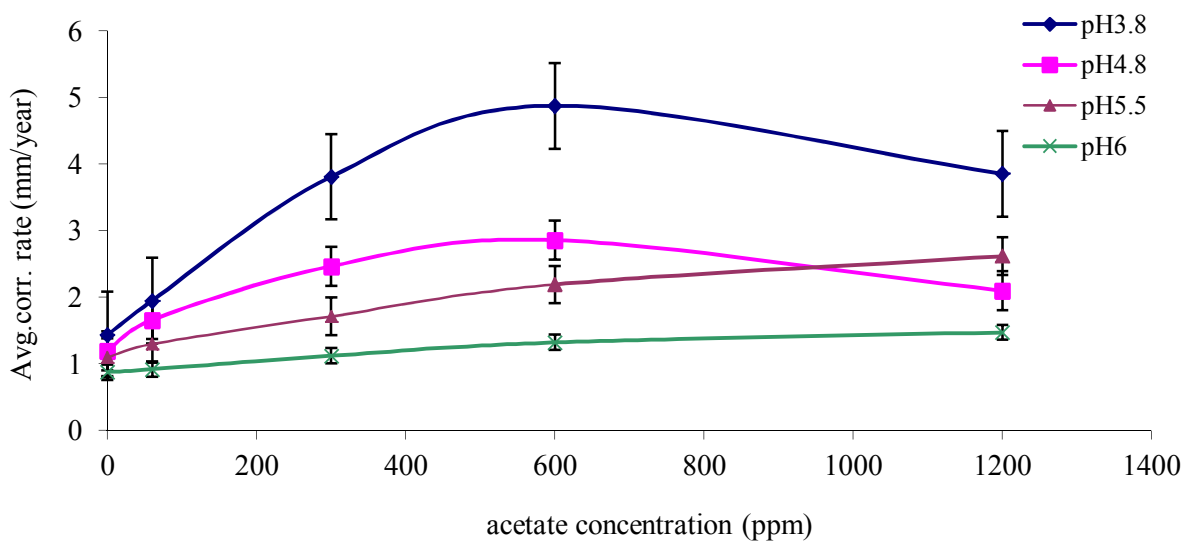


Figure 6 Average corrosion rate (mm/year).vs. acetate concentration (ppm) with CO₂ at different pHs

3.1.2. The Overall Effect Of Total Acetate With N₂ On Corrosion of Mild Steel

Figure 7 shows comparison of the variation of corrosion rate with acetate concentrations with nitrogen for different pHs. From this plot can observe that for all pHs the corrosion rate is higher when adding more acetate and the highest corrosion rate is obtained at pH 3.8. However, the corrosion rate has maxima at 600 ppm for both solutions of the pH 3.8 and the pH 4.8, and slightly decrease at 1200 ppm.

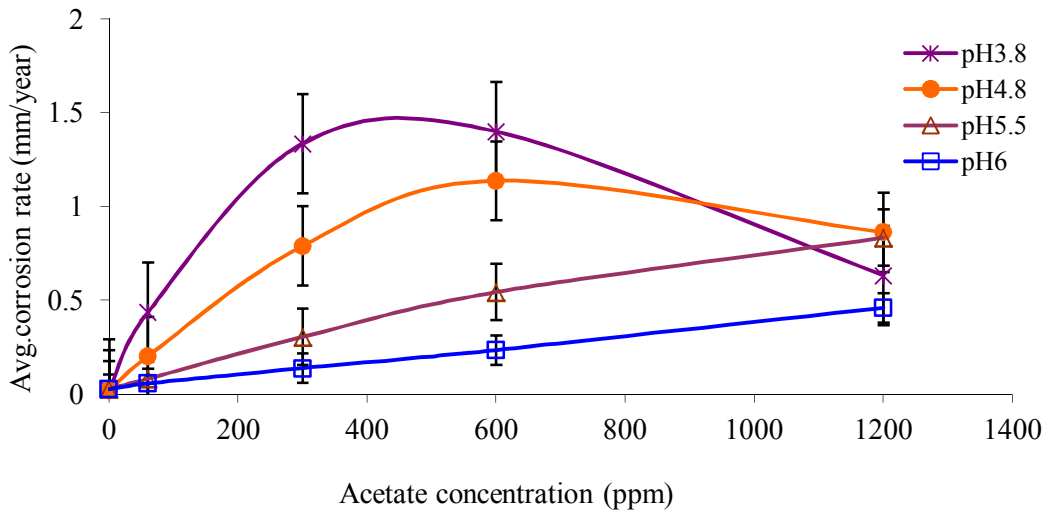


Figure 7 Average corrosion rate (mm/year).vs. acetate concentration (ppm) with N₂ at different pHs

3.2. Effect Of Total Acetate On CO₂ Corrosion

Figure 8 illustrates the relationship between the average corrosion rate (mm/year) and total acetate concentration ppm at pH 3.8. The corrosion rate increases with increased acetate concentration. The maximum corrosion rate obtained at 600 ppm acetate is about 4.8 mm/year,

3 times more than CO₂ only, and then the corrosion goes down with increased acetate. However, if we compare the corrosion rate which is caused by acetate saturated with CO₂ experimentally with corrosion rate by calculating corrosion rate caused by CO₂ only plus corrosion rate caused by acetate with nitrogen, we can observe that at low acetate concentration, 60ppm, they are close together, but with increased acetate the gap between them increases and the corrosion rate which is caused by acetate saturated by CO₂ experimentally is more than calculated by addition of the CO₂ and acetate effects.

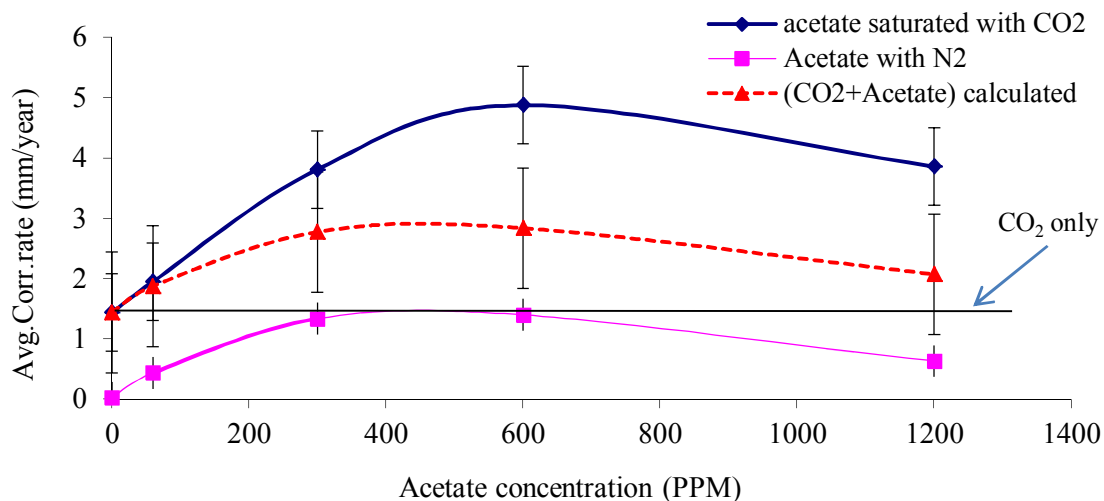


Figure 7 Average corrosion rate(mm/year).vs. acetate concentration (ppm) with CO₂ & N₂ at pH 3.8

Figure 8 shows the results of the average corrosion rate at different acetate concentration for mild steel in 3% NaCl, CO₂ saturated solution with different concentration of acetate and acetate with nitrogen at pH 4.8. The general effect of the total acetate can clearly be seen here, the line, which represents acetate saturated with CO₂, is the one has the high corrosion rate. However, the corrosion rate increase with increase acetate

concentrations, and maximum rate obtained at 600ppm acetate is about 2.9 mm/year, but at higher acetate concentration the corrosion rate decreases. on the other hand, if we compare the corrosion rate which caused by acetate with CO₂ experimentally with that calculated from acetate with nitrogen plus CO₂ only, it can be seen that they are not the same, and the rate in acetate saturated with CO₂ experimentally is more than calculated by addition of the CO₂ and acetate effects, except at 1200 ppm acetate where they are close together. This difference is due to some interaction between acetate and CO₂ to gives high corrosion rate.

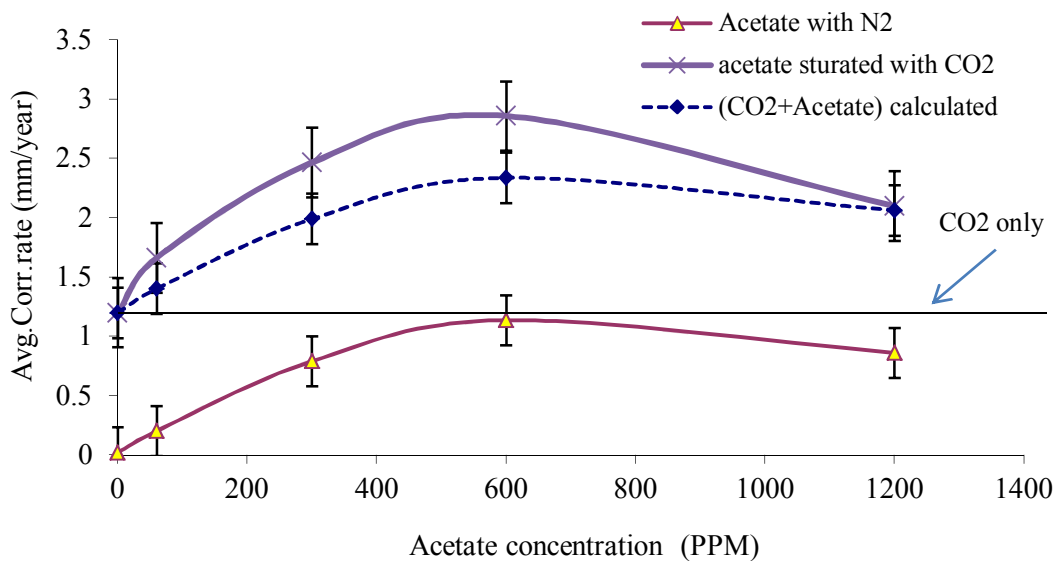


Figure 8 Average corrosion rate (mm/year).vs. acetate concentration (ppm) with CO₂& N₂ at pH4.8

4. CONCLUSION:

- 1) It is clear from the results (figures 2,3,4 and 5) that for mild steel in CO₂ solution (without acetate), high corrosion rates were measured at pH 3.8, about 1.44 mm/year.

- 2) The corrosion rate of CO₂ corrosion is affected by addition of acetate. 60 ppm acetate increases the corrosion rate about 2 times compared to the system saturated with CO₂ only at pH 3.8 and pH 4.8.
- 3) At 600 ppm acetate with CO₂ and pH 3.8 the maximum corrosion rate is obtained. The corrosion rate is raised almost 3 times when compared with the value obtained in the CO₂ only, from a value around 1.44 mm/year to almost 4.8 mm/year.
- 4) The greater amount of acetate or acetic acid at low pHs the higher corrosion rate obtained expect the highest concentrations, and the corrosion rate decreases with increased pH. We expected this because at higher pHs there are few H⁺ ions in the solution, and the dominant cathodic reaction is H₂CO₃ reduction, and there is low acetic acid concentration at high pHs.
- 5) The mechanism by which HAC increases the corrosion rate possibly explained by it is ability to both decrease the surface pH and solubilise of Fe²⁺, thus reducing the iron carbonate film thickness.
- 6) At higher acetate and acetic acid concentration at pH 3.8 & pH 4.8 there was a reduction in corrosion rate, as the time increased. We attribute this behaviour to inhibition by acetate or acetic acid, which needs further investigation.
- 7) The addition of the contribution of the corrosion effect from CO₂ only and acetate or acetic acid only does not represent the exact behaviour of the acetic acid or acetate saturated with CO₂. This may lead to some interaction between the acetic acid or acetate with CO₂ to give higher corrosion rate, so calculation of corrosion rate by addition of the CO₂ and acetate or acetic acid is not valid.

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