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Study Combinations Effects of HAc in H₂S/CO₂ Corrosion

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Abstract: In oil and gas production environment, CO₂, H₂S and Acetic Acid (HAc) have become a main source that affect corrosion to the carbon steel and cause failures on the facilities. In order to minimize the failures, there must be a tool to predict those failures. This research proposed a prediction model incorporated with H₂S and HAc in CO₂ environments using a set of experiments. The experiments were conducted in the 3% NaCl solution saturated with 300 ppm of H₂S in CO₂ gas. LPR and EIS methodology were used to study corrosion mechanism and to calculate carbon steel corrosion rate. The results revealed that effects of H₂S and HAc in CO₂ environment have contributed in increasing corrosion rate. Those effects were caused by additional of cathodic activation reactions in the system as described by scan polarization. Analyzing through EIS showed that combined effect of CO₂ and H₂S promote to form film formation indicated by Warburg diffusion spectra. Although interaction of CO₂ and H₂S gas has a capability to produce film formation, the film can not inhibit corrosion reaction that may relate to the presence of HAc in the solution.

Key words: CO₂/H₂S corrosion, LPR, EIS

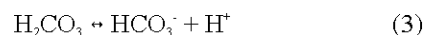
INTRODUCTION

Crude oil is a complex mixture of hydrocarbons species which determines oil characteristics. Analytical data shows that components in crude oil varied with main components classified as: carbon, hydrogen, nitrogen, sulfur and their compounds. Studies have demonstrated that those multi species factors can govern the corrosion process in many ways and in several mechanisms (Joosten and Hembree, 2002; Amri *et al.*, 2008). Many efforts have been made for understanding CO₂/H₂S corrosion mechanism to improve the predictions. But, to date, the reported model available does not represent combining parameters such as HAc, H₂S and CO₂. There are limited studies in the literature to observe those mixed effects.

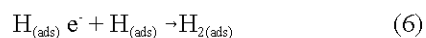
CO₂ corrosion: In the CO₂ corrosion of carbon steel, basically, there are two main corrosion mechanisms which are cathodic reactions and anodic reaction. In cathodic site CO₂ dissolves to the water phase and hydrates to form carbonic acid as follows (Nordsveen *et al.*, 2003; Gray *et al.*, 1990):



Carbonic acid dissociates into further reactions which depends on pH. At pH 4 or lower carbonic acid dissociates into bicarbonate ions and carbonate ions in two steps (Parakala, 2005):



It was suggested that H⁺ ions are dominant species promoting corrosion. H⁺ ions are able to diffuse to the metal surface through boundary layer. On the metal surface, H⁺ ions involve in hydrogen evolution reaction. These additional charge transfer reactions are suggested as factors governing the corrosion rate (Parakala, 2005):



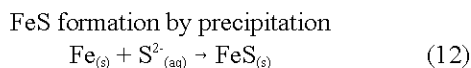
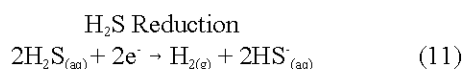
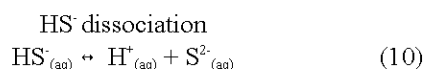
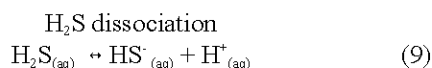
On anodic site, The mechanism of anodic reaction is the oxidation reaction to form ferrous (Fe²⁺) ions. The general reaction process is:



Nesic *et al.* (1996) reported that the presence of CO₂ does not have any effects on the anodic dissolution of

iron. Iron dissolution kinetics in CO₂ environment involves chemical ligand that adsorbs at the metal surface and catalyzing the dissolution of iron.

H₂S corrosion mechanism: Hydrogen sulfide is weakly acidic, when dissolved in water, H₂S is involved in a series of chemical reactions:

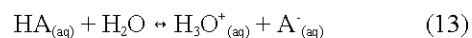


The role of H₂S in changing behavior of corrosion rate was studied by Brown (2004). In his experiment, he found that small concentration of H₂S (less than 30 ppm) with CO₂ saturated in water, corrosion rate will increase compare with no H₂S. However, corrosion rate will decrease when he conducted a series of variable as; 15 % NaCl, 7, 9 bar total pressure, 100 ppm of H₂S concentration, pH solution < 5. It happened in single phase and multi phase flow.

Anderko and Robert (1999) reported that the corrosion rate drops significantly for partial pressures of H₂S ranging from 2.10⁻⁶ to 10⁻⁴ atm and reaches a plateau in a relatively wide range of H₂S partial pressures above 10⁻⁴ atm. Reduction in corrosion rates has been reported when the H₂S partial pressure exceeds 10⁻³ atm in some systems. At substantial H₂S partial pressures (above 10⁻² atm), the aqueous H₂S, and HS⁻ species become sufficiently to increase in the corrosion rate.

Acetic acid corrosion mechanism: Acetic Acid (HAc), structural formula is represented as CH₃COOH. It is a weak acid which is not completely dissociated in aqueous solutions. It has been reported that free acetic acid can increase corrosion rate (Veloz, 2002; Ismail *et al.*, 2006). Mechanism of dissolved acetic acid in CO₂ corrosion can be correlated to the concentration of undissociated HAc present in the brine (George and Nesic, 2007). The dissociated of the acid can modify the corrosion rate in the CO₂ corrosion rate has been validated with laboratory

tests by (George and Nesic, 2007). The dissociation process of acetic acid in water is given by (Nafday, 2004):



The aqueous of HAc, then partly dissociation into hydrogen and acetate ions:



The reaction mechanism and kinetics of the overall reactions are influenced by acetic acid concentration, CO₂ partial pressure, pH and water contaminants. The effect of HAc on the corrosion of mild steel has been studied by a number of experimental results. Crolet (1999) make the point that CO₂ induced acidification also can cause partial re-association of anions. Such weak acids then will increase the oxidizing of H⁺ by raising the limiting diffusion current for cathodic reduction. The presence of this acid also will tend to solubilise the dissolving iron ions.

Other effects of HAc are that it decreases pH, increasing the cathodic limiting current, and decrease E_{corr}. In this condition, the cathodic reaction will become the rate determining step. The limitation is due to diffusion of proton to the steel surface rather than electron transfer. There was an agreement that HAc can increase the cathodic reaction rate (hydrogen evolution reaction (Crolet, 1999).

Garsany *et al.* (2002) argued that the increase of corroisn rate of HAc in CO₂ environment must be proportional to the concentration of undissociated acetic acid in the brine. They emphasized that the electrochemistry of acetic acid at steel cannot be distinguishable from free proton (because of its rapid dissociation). The work of Crolet (1999) suggested that the presence of HAc inhibited the anodic (iron dissolution) reaction at this inversion point, HAc is the predominant acid compared to carbonic acid and is therefore the main source of acidity.

Experimental set-up:

Specimen preparation and test matrix: The working electrodes were carbon steel and the chemical composition is as shown in Table 1. The cylindrical specimens have diameter of 12 mm and 10 mm length.

Before immersion, the specimen surfaces were polished successively with 240, 400 and 600 grit SiC paper, rinsed with methanol and decreased using acetone.

Table 1: Composition of 080A15 carbon steel used in the experiments

Steel	C (%)	Si (%)	Mn (%)	P (%)	S (%)	Cr (%)	Ni (%)
080A15	0.14	0.175	0.799	0.01	0.03	0.06	0.065

Table 2: Experimental matrix used in the test

Steel type	080A15 (BS 970)
Aqueous solution	Oxygen-free, 3 wt% NaCl
Purged gas	CO ₂ , N ₂ , CO ₂ /H ₂ S (300 ppm)
Total pressure	Atmospheric
HAc concentration	0 to 340 (ppm)
Temperature	22 to 80°C
Rotation rate	Static
pH	4
Measurement techniques	Potentiodynamic Sweeps (PS), Linear Polarization Resistance (LPR), Electrochemical Impedance Spectroscopy (EIS)

Table 3: Gas composition used in the experiments.

CO ₂ (bar)	H ₂ S (mbar)	N ₂ (bar)	H ₂ S (ppm)	CO ₂ (ppm)	CO ₂ /H ₂ S
0.7	0.3	0.2997	300	700000	2333

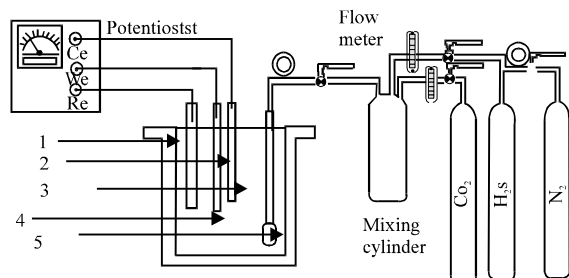


Fig. 1: Experimental arrangement for static test, 1 Glass cell, 2: Reference electrode, 3: Counter electrode, 4: Working electrode, 5: CO₂ gas bubble

The experiments were repeated at least twice in order to ensure reasonable reproducibility. The test matrix used to do the experiment is presented in Table 2.

Static test set-up: The typical experimental arrangement for the static test is illustrated in Fig 1. The test assembly consisted of one-litre glass cell bubbled with CO₂. 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 Ag/AgCl and the auxiliary electrode was a platinum electrode. The Linear Polarization Resistance (LPR) technique was used to measure the corrosion rate. The procedure was similar to ASTM Experimental test G 5-94 (ASTM, 2004).

Cell solutions: The experiments were performed in stagnant condition. The total pressure was one bar, the glass cell was filled with one liter of distilled water with 3% wt NaCl which was stirred with magnetic stirrer. Then,

CO₂ or CO₂/H₂S/N₂ gas was bubbled through the cell (at least one hour prior to experiments) in order to saturate and de-aerates the solution. After the solution was prepared, the pH was adjusted to reach the pH set by using NaHCO₃ as buffer solutions. During the experiment, constant concentration of gases was continuously bubbled through the electrolyte in order to maintain consistent water chemistry.

Gases compositions: The gas mixtures comprising 300 ppm H₂S balanced with nitrogen was obtained commercially from MOX®. The mixture of H₂S balanced with N₂ and CO₂ was adjusted using gas regulator and flow meter purged to the glass cell through mixing tube. The compositions of mixed gases planned were as follows (Table 3).

RESULTS AND DISCUSSION

Corrosion rate of carbon steel at varying HAc concentration in CO₂/H₂S system studied by LPR and EIS technique is presented in Fig. 2. In the experimental condition with HAc concentration ranged from 0-18 ppm, the presence of HAc increased corrosion rate consistently. In other word, HAc controlled the corrosion rate. HAc increased corrosion rate by 0.5 times with addition of 180 ppm of HAc.

In order to study surface characteristics of H₂S/CO₂/HAc corrosion, it was studied using EIS technique as presented in Fig. 3. In Fig. 3, It demonstrates characteristics of the Nyquist plots of 80 and 130 ppm of HAc concentration in saturated 300 ppm H₂S/CO₂ solution. As can be seen from the Fig. 3. The impedance diagram showed a depress semi-circle at high frequencies which indicating a double layer capacitance. This condition, as quoted by Bai *et al.* (2006) was suggested as there were heterogeneous surface and the non-uniform distribution of current density.

With the addition of 80 and 180 ppm HAc, the steady state impedance diagram demonstrated a smaller depressed semi-circle with similar characteristic. The decrease in polarization resistance R_p from EIS measurements indicated the increase in corrosion rate with increasing HAc concentration. Moreover, there was a tail observed in the experiments (Fig. 3). These results suggested that the mechanism is under diffusion process control in the presence of HAc. The same characteristic was found in the experiments without HAc. From the Fig. 3 description, it can be concluded that the corrosion reaction of H₂S/CO₂ system was dominated by HAc reactions.

From the EIS data, it can also be described several values of solution resistance, charge transfer resistance,

Table 4: Circuit parameters values for representing EIS experimental data.

El. circuit	Blank	80 (ppm)	130 (ppm)
Rp (ohms.cm ²)	104	88	74
C (F)	3.32E-03	6.18E-03	6.92E-03
Depression angle	30.56	38.23	35.23
Corr. Rate (mm year ⁻¹)	1.25	1.49	1.56

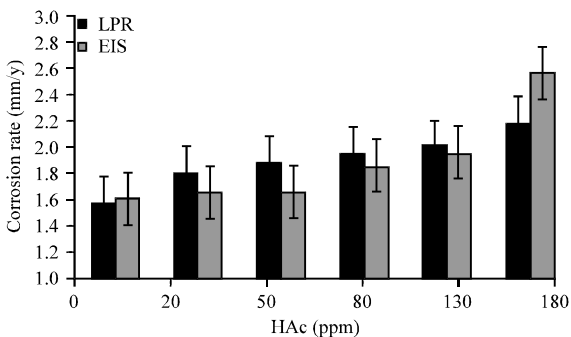


Fig. 2: Corrosion rate at varying HAc concentration at conditions: total pressure 1 bar, 0.7 bar CO₂, 0.3 mbar H₂S, 22°C. (Comparison between LPR and EIS results)

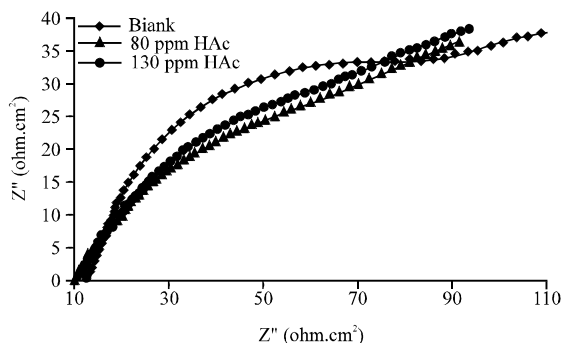


Fig. 3: Nyquist plot to calculate corrosion rate as a function of HAc concentration at conditions of total pressure 1 bar, 0.7 bar CO₂, 300 ppm H₂S, 22°C

capacitance film formed and corrosion rate in the form of equivalent circuit parameters as presented in Fig. 4.

Table 4 showed the parameters values of solution resistance, charge transfer resistance, capacitance film formed and corrosion rate which was obtained from the experiments using EIS technique.

From the equivalent values, it demonstrated a decreased of charge transfer resistance with the increased of HAc concentration. It means that corrosion rate increased as concentration of acetic acid was added (Fig. 3). The effect is proportional to the amount of HAc added. As shown in Fig. 3, the charge transfer resistance decreased from 104 to 74.

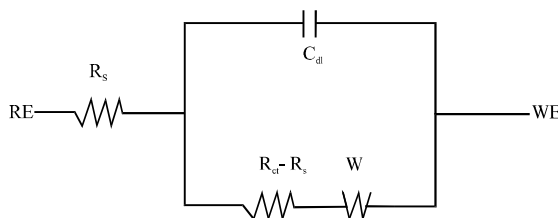


Fig. 4: Typical equivalent circuit for a mixed diffusion and charge transfer control used to represent the experimental conditions

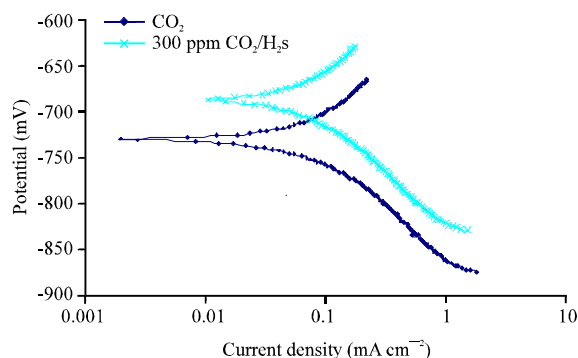


Fig. 5: Potentiodynamic sweeps in CO₂ solution with/without H₂S. (Total pressure 1 bar, temperature 22°C, pCO₂ 0.7 bar, pH₂S 0.3 mbar, pH 4 and stagnant)

The polarization sweeps were conducted to study effect of H₂S on CO₂ corrosion. The result is presented in Fig. 5. From the figure showed that there were differences between polarization graph of carbon steel corrosion in CO₂ and in 300 ppm H₂S/CO₂ system. H₂S gas increased CO₂ corrosion rate and also increase cathodic Tafel slope. This finding was also observed by Zhang and Cheng (2009), when they conducted experiments in condition with a constant H₂S/CO₂ partial pressure ratio of 1.7.

Kvarekval (1999) explained that the increased corrosion rate was caused by sulfide ions or by H₂S acting as a catalyst for hydrogen evolution and govern diffusion proton donors. Further, He reported that H₂S can also increase the hydrogen evolution rate without taking part in the net reaction. In further analyses, these H⁺ ions concentrations from H₂S molecule can penetrate on steel surface to create a pitting corrosion which can increase corrosion rate.

In addition, additional of H₂S also gave impact on diffusion limiting current density of CO₂ corrosion. As can be seen from experiments using EIS technique (Fig. 3), there was tail in the Nyquist plot which indicates mass transfer effect in the process. However, from the scan polarization analyses, it showed activation reaction

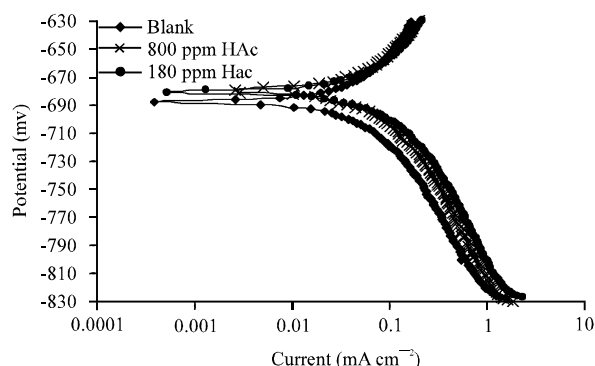


Fig. 6: Potentiodynamic sweeps in 300 ppm $\text{H}_2\text{S}/\text{CO}_2$ saturated solution at various HAc concentrations. (Temp. 22°C , Total pressure 1 bar, pCO_2 0.7 bar, pH_2S 0.3 mbar, pH 4, stagnant)

control reaction. Thus, the behavior of cathodic limiting current density consisted of chemical reaction and diffusion process.

Effects of addition of HAc on potentiodynamic test in Fig. 6. Figure 6 indicated that there was no significant effect of addition of HAc on anodic Tafel slopes in 300 ppm $\text{H}_2\text{S}/\text{CO}_2$ system. However, the cathodic slope showed an increase of reaction process in the presence of HAc. Figure 6 also revealed that anodic polarization behavior did not change significantly with the additional of hydrogen sulfide. Anodic tafel slope was consistence with iron dissolution in CO_2 solution. However, cathodic Tafel slope have increased significantly. It means that HAc was a the dominant factors that govern the reaction process.

CONCLUSIONS

- In the presence of 0.3 mbars of H_2S in 0.7 bars of CO_2 , the average corrosion rate increased approximately 10% compared to free H_2S
- The H_2S accelerate corrosion rate by increasing cathodic Tafel slope
- The introduction of HAc to 180 ppm in the $\text{H}_2\text{S}/\text{CO}_2$ mixture gases caused corrosion rate increased
- The anodic polarization behavior did not change significantly with the additional of hydrogen sulfide
- HAc was a the dominant factors that govern the reaction process in $\text{CO}_2/\text{H}_2\text{S}$ system. Behavior of cathodic reaction consisted of chemical reaction and diffusion process

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