

CO₂ Corrosion Mechanism of Carbon Steel in the Presence of Acetate and Acetic Acid

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The corrosion behavior of carbon steel (N80) in carbon dioxide saturated 1%NaCl solution with and without acetic acid or acetate was investigated by weight-loss test, electrochemical methods (polarization curve, Electrochemical impedance spectroscopy). The major objective is to make clear that the effect of acetic acid and acetate on the corrosion of carbon steel in CO₂ environments.

The results indicate that either acetic acid or acetate accelerates cathodic reducing reaction, facilitates dissolution of corrosion products on carbon steel, and so promotes the corrosion rate of carbon steel in carbon dioxide saturated NaCl solution. All Nyquist Plots are consisting of a capacitive loop in high frequency region, an inductive loop in medial frequency region and a capacitive arc in low frequency region. The high frequency capacitive loop, medial frequency inductive loop and low frequency capacitive arc are corresponding to the electron transfer reaction, the formation/adsorption of intermediates and dissolution of corrosion products respectively. All arc of the measured impedance reduced with the increase of the concentration of Ac⁻, especially HAc. However, the same phenomenon is not notable after reducing pH value by adding HCl. HAc is a stronger proton donor and can be reduced directly by electrochemical reaction firstly. Ac⁻ can't participate in electrochemistry reaction directly, but Ac⁻ an hydrate easily to create HAc in carbon dioxide saturated environments. HAc is as catalyst in CO₂ corrosion. As a result, the corrosion rate was accelerated in the presence of acetate ion even pH value of solution increased.

Keywords : CO₂ corrosion, carbon steel, acetic acid, acetate, mechanism

1. Introduction

Carbon dioxide (CO₂) corrosion has been one of the major problems associated with oil and gas production since been discovered in 1940.¹⁾ Many workers have studied the mechanism and protections of CO₂ corrosion widely,^{2,10)} which was including the effect of HAc in carbon dioxide Solution.¹¹⁾ Crolet and Bonis¹²⁾ pointed out the need for a complete water analysis which must specify the concentration of bicarbonate, acetate and Ca²⁺. They found the presence of acetate ions greatly increased the diffusion limited reduction of protons; Garsany, Pletcher and Hedges¹³⁾ had reemphasized the key role for the equilibrium concentration of acetic acid in the brine in determining the rate of steel corrosion, they proposed that the role acetic acid in the brine in determining the rate of steel corrosion; Hedges and McVeigh¹⁴⁾ carried out a series of CO₂ corrosion tests simulating the Wytch Farm flow line conditions to study the effect of bicarbonate and acetate

ions on the corrosion rate; Y. Sun, K. George and S. Nestic¹⁵⁾ studied the effect of Cl⁻ and acetic acid on Localized CO₂ Corrosion in Wet Gas Flow. Though some information concerning the electrochemical behavior and the mechanism of enhanced corrosion had been reported in the presence of Acetic Acid in literature,^{16,17)} the corrosion mechanism when existing acetic acid in CO₂ corrosion had not been understood well, for example, acetic acid can change the anodic dissolution processes or acetic acid only affect corrosion product film to enhance corrosion rate. In fact, in CO₂ corrosion environments, from field experiences, the corrosion rate of carbon steel increased when Ac⁻ ions are present in the produced liquids, though acetate can increase pH of the liquid. This observation was contrary to most models for CO₂ corrosion prediction.¹¹⁾ Laboratory research has shown that both HAc and Ac⁻ can increase the corrosion rate of iron.^{14,16)} In this work, the effect of HAc and Ac⁻ on corrosion behavior in CO₂ saturated 1%NaCl solution at 0.1 MPa CO₂, 50°C had been investigated by weight loss, potentiodynamic polarization, EIS (electrochemical im-

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pedance spectroscopy) measurement. The attention was focused on CO₂ corrosion mechanism in the presence of acetate and acetic acid, especially the mechanism of anodic dissolution process.

2. Experimental Procedure

2.1 Materials and Test Solutions

The test specimens (50×10×3mm) and the working electrodes (S=1cm²) were prepared from N80 carbon steel, the chemical composition is: C 0.23, Si 0.22, Mn 1.35, P 0.017 S 0.012, Ni 0.02, Mo 0.01 Cr 0.05. The test solution was 1% NaCl which was prepared by NaCl (chemical grade) and distilled water. The test solution was saturated with CO₂ by purging for one hour prior to testing. Chemical grade acetic acid (HAc) and sodium acetate (NaAc) were used for adjusting the acetate concentration of the test solutions.

2.2 Weight-loss Tests

Weight-loss tests were carried out using a static autoclave. The test specimens were mechanically polished using silicon carbide paper (up to 1200 grit), cleared with distilled water, and then degreased in ethanol and acetone. The test specimens were mounted in a cage, 1.0 liter of saturated 1% NaCl solution was poured into the vessel of autoclave, and then the autoclave was closed. More deaeration was carried out by the operation of CO₂ gas bubbling for one hour. CO₂ gas was then charged to test pressure. The test temperature and pressure were 50°C and 0.1 MPa, and the test time was 24 hours. In each autoclave test, three samples were simultaneously exposed to the corrosive solution. After test, coupons were removed from the test solution, washed in 10 % (wt) hydrochloric acid solution with inhibitor and cleared by ethanol, then dried for 24 hours to weigh.

2.3 Electrochemical Measurements

Electrochemical measurements were carried out in a glass cell at 50°C and 0.1MPa CO₂. Polarization curves were measured with a scanning rate 0.33 mV/s; the scanning potential was ±200 mv vs. corrosion potential. EIS data were obtained using IM6e electrochemical workstation at frequencies 10⁵~5×10³Hz, and the amplitude of sinusoid ac voltage signal was ±5 mV. The fitting of EIS data was carried out using Zview2 software. A saturated calomel electrode (SCE) was used as reference electrode. Platinum bar served as an auxiliary electrode.

3. Results and Discussion

3.1 Weight-loss Tests

The results of weight loss tests are summarized in Table 1. Whether adding HAc or NaAc, the corrosion rate of N80 steel increase with increasing Ac- concentration. In addition, the corrosion rate in the case of adding HAc is higher than that in the cases of adding NaAc at same Ac- concentrations. When Ac- is added, the solutions pH values would be changed. The pH value of solutions was measured using a pH indicator. The results also are summarized in Table 1. As shown in Table 1, acetic acid is weak acidic and could decrease pH value; acetate is weak alkaline and could increase pH value. Obvious, HAc or Ac will affect the corrosion rate of carbon dioxide corrosion. HAc is a stronger acid than carbonic acid, when HAc is coexisting with carbonic acid, it will be firstly depleted. For example, if 36 ppm HAc (6×10⁻⁴ol) was added, HAc will be consumed completely as cathodic reaction, and 3×10⁻⁴ 4mol Fe will be dissolved as Fe²⁺ by the anodic reaction, the reactive mass of Fe is: 3×10⁻⁴×56= 1.68×10⁻² g. Since three pieces of samples were exposed to the solution, and each surface area is 13.60 cm², the density of Fe is 7.8 g/cm³, so the corrosion rate of N80 steel will be calculated:

$$V_{wl} = \frac{W_0 - W_1}{S_0 t} (\text{g} \cdot \text{m}^{-2} \cdot \text{h}^{-1}) = \frac{1.68 \times 10^{-2}}{3 \times 13.6 \times 10^{-4} \times 24}$$

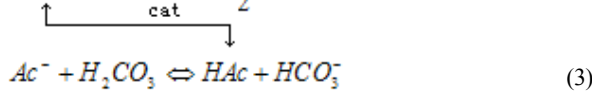
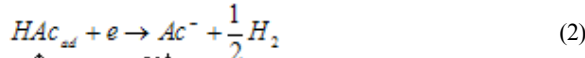
$$\text{g} \cdot \text{m}^{-2} \cdot \text{h}^{-1} = 1.72 \times 10^{-1} \text{ g} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$$

$$D = \frac{V_{wl} \times 8.76}{d} (\text{mm} \cdot \text{a}^{-1}) = \frac{1.72^{-1} \times 8.76}{7.8} = 0.193 \text{ mm} \cdot \text{a}^{-1}$$

Table 1. Weight-loss results of N80 steel in CO₂ saturated 1%NaCl solution with and without NaAc (or HAc) at 0.1MPa CO₂, 50°C

Experimental conditions	Ac Concentration (ppm)	V_{corr} (mm/y)	pH Measure d
1%NaCl 0.1MPa CO ₂ ,50°C, 24 hours Ac (Add as NaAc)	0	0.396	4.09
	36	0.421	4.52
	72	0.428	4.80
	360	0.430	5.20
1%NaCl 0.1MPa CO ₂ ,50°C, 24 hours Ac Add as HAc)	0	0.396	4.09
	36	1.040	3.99
	72	1.390	3.86
	360	2.474	3.45

The corrosion rate is 0.396 mm/a without HAc, Obvious, 0.193+0.396=0.589 mm/a <1.040 mm/a, so it can deduct that HAc is as catalyst in CO₂ corrosion. The reaction mechanism maybe considered as following



As shown in Table 1, when acetate was added (as NaAc), though the most added Ac⁻ was being in HAc in this condition, the enhanced corrosion rate was lower observably than that in the case of adding HAc. This implied that HAc catalysis was dependent on pH of the media.

3.2 Polarization Curves

Fig. 1 shows the polarization curves of N80 steel in CO₂ saturated 1%NaCl solution with different concentration of Ac⁻ (added NaAc or HAc). In all cases, an active dissolution characteristic appeared in the anodic part of the polarization curves, but the cathodic curves are different; there is a diffusion process-like current shoulder in the cathodic part of the polarization curves, which arose from inhomogeneous reaction of CO₂ hydration on electrode surface in CO₂ saturated environments.¹⁸⁾ When NaAc or HAc was added, the cathodic polarization current shoulder increased because the reduction reaction was enhanced by directly reducing HAc adsorbed on electrode surface, and the adsorption process of HAc on electrode surface maybe become a rate determining step. The cathodic reaction as follows when HAc is present in solution

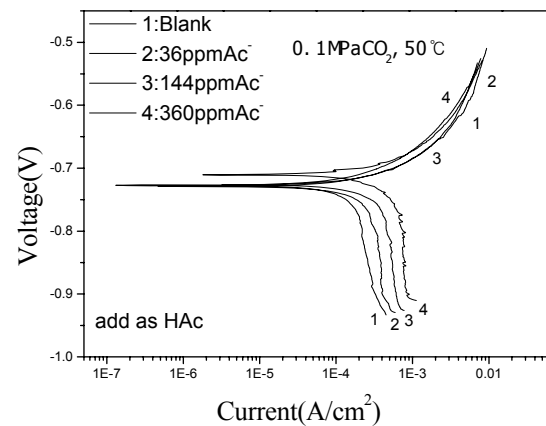
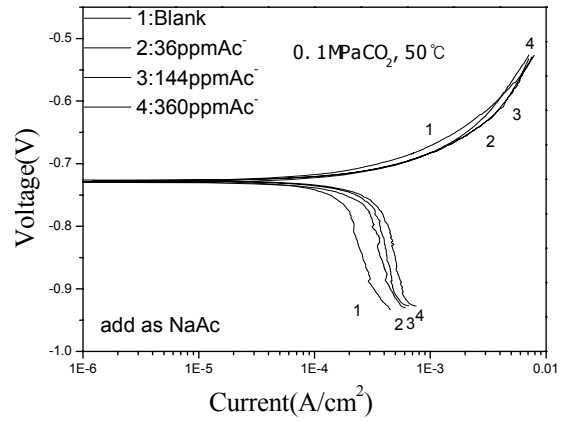


Fig. 1. The polarization curves of carbon steel in CO₂ saturated 1%NaCl solution with different concentrations of NaAc (or HAc) at 0.1 MPa CO₂, 50 °C

¹⁴⁾ (In added NaAc case: $Ac^-_{aq} + H_2O \rightleftharpoons HAc_{aq} + OH^-_{aq}$).



Table 2. Fitting parameters of polarization curves for N80 steel in CO₂-saturated 1%NaCl solution with and without different concentrations of Ac⁻(added as NaAc or HAc)

Experimental Condition	Ac ⁻ Concen. (ppm)	E _{cor} (mV)	ba (mV)	bc (mV)	icor (mA/cm ²)	Corrosion rate (mm/a)
0.1MPa, 50 °C, Ac (Add as NaAc)	0	728	90	464	0.1499	1.75
	36	727	93	418	0.2002	2.34
	144	726	94	417	0.2450	2.87
	360	724	102	348	0.2605	3.05
0.1MPa, 50 °C, Ac (Add as HAc)	0	728	90	464	0.1499	1.75
	36	728	92	400	0.2118	2.48
	144	725	99	383	0.3018	3.54
	360	710	104	276	0.3707	4.34



The fitting parameters are summarized in Table 2. E_{cor} is corrosion potential; b_a and b_c are the apparent anodic and cathodic Tafel slopes respectively; i_{corr} is corrosion current density. As shown in Table 2, there was a positive shift in E_{cor} and an increase in i_{corr} with the increase of concentration of acetic acid or acetate; b_a increases, but b_c decreases with the increase of concentration of acetic acid or acetate. The result implied that whether adding HAc or NaAc, the cathodic reduction process was enhanced, so corrosion rate of N80 steel was accelerated.

3.3 EIS Measurements

Fig. 2(a) and Fig. 2(b) show the measured EIS of N80 steel in CO_2 -saturated NaCl solution with different concentration of Ac^- (added HAc or NaAc) at anodic polarization potential. At anodic polarization potentials, EIS mostly responded to the anodic dissolution process.¹⁹⁾ As shown in Fig. 2(a) and Fig. 2(b), all Nyquist Plots are consisting of a capacitive loop in high frequency region, an inductive loop in medial frequency region and a capacitive arc in low frequency region. The high frequency capacitive loop, medial frequency inductive loop and low frequency capacitive arc are corresponding to the electron transfer reaction, the formation/adsorption of intermediates and dissolution of corrosion products respectively. All arcs contracted with the increase of the concentration of Ac^- , especially when HAc was added. Because HAc, Ac^- or H^+ can affect the anodic dissolution process, so a serial of experiment must be performed to distinguish the effect of H^+ and Ac^- . Fig. 2(c) shows the measured EIS of N80 steel in CO_2 -saturated NaCl solution at anodic polarization potential, and the solution pH was adjusted only using HCl.

The electrode equivalent circuit for the EIS measured at anodic polarization potentials is shown in Fig. 3. Where, R_l and $CPE1$ are the solution resistance between reference and working electrode and a constant phase element corresponding to double layer of electrode respectively; R_t , R_{at} , L , R_s and $CPE2$ are electron transfer resistance of anodic reaction, resistance and inductance corresponding to the formation/adsorption of intermediates, resistance and constant phase element corresponding to the dissolution of corrosion products. Fitting parameters of EIS are shown in Table 3. All resistances decrease with increasing Ac^- concentrations. R_{at} corresponding to formation/adsorption of intermediates is biggest and most obviously change with Ac^- concentrations; R_t and R_s Changed remarkably with Ac^- concentration too. When change pH value only using

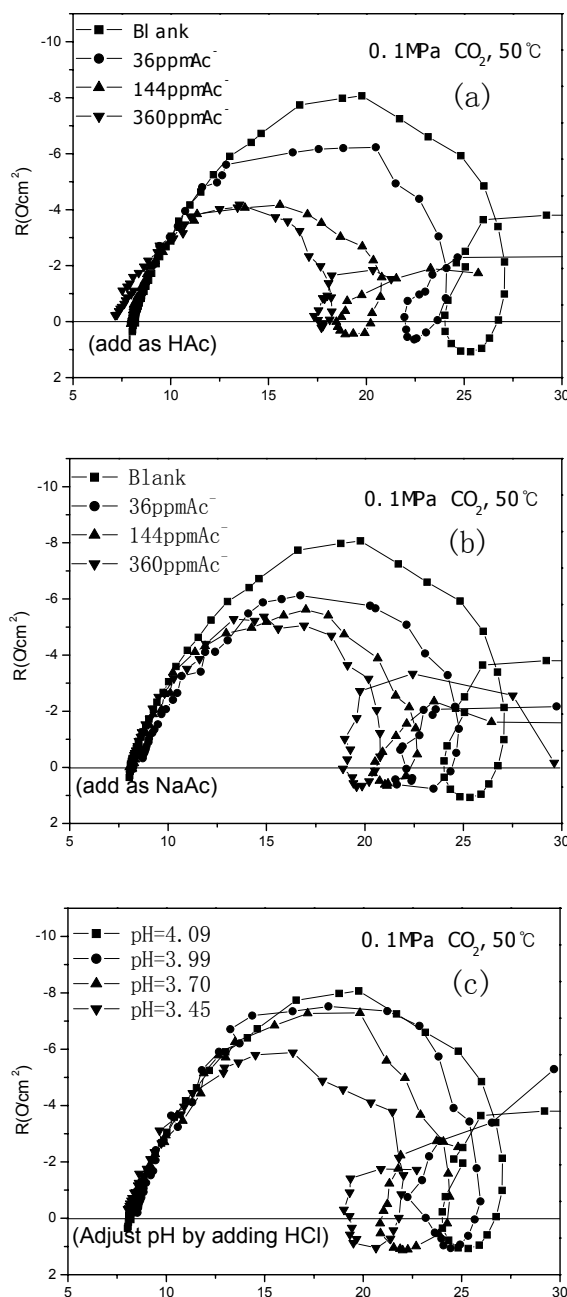


Fig. 2. The impedance of N80 steels measured in CO_2 -saturated 1%NaCl solution with different concentrations of NaAc (or HAc) at 0.1MPa CO_2 50 °C

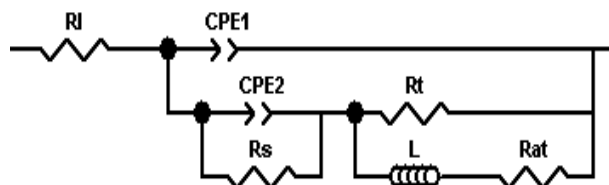


Fig. 3. The equivalent circuits of the electrodes at anodic polarization potential ($\Delta E = +50mV$)

Table 3. Fitting parameters of EIS for N80 steel in CO₂-saturated 1%NaCl solution at anodic polarization potential $\Delta E = +50\text{mV}$ (50 °C, 0.1MPa CO₂)

Experimental Condition	CPE1-T (F/cm ⁻²)	CPE1-P	CPE2-T (F/cm ⁻²)	CPE2-P	Rs (Ω)	Rt (Ω)	L (H/cm ⁻²)	Rat (Ω)	
Ac- Concen. (ppm) (add as NaAc)	0 (pH=4.09)	9.66×10 ⁻⁴	0.7608	1.787	0.9976	8	22	4.4	61
	36 (pH=4.52)	9.62×10 ⁻⁴	0.7794	1.464	0.9996	6	18	4.1	60
	144 (pH=4.97)	9.87×10 ⁻⁴	0.7975	1.331	0.9987	5	17	4.1	55
	360 (pH=5.20)	9.09×10 ⁻⁴	0.7972	1.445	0.9676	4	16	3.0	50
Ac- Concen. (ppm) (add as HAc)	0 (pH=4.09)	9.66×10 ⁻⁴	0.7608	1.787	0.9976	8	22	4.4	61
	36 (pH=3.99)	7.14×10 ⁻⁴	0.7744	1.241	0.9596	5	17	3.9	58
	144 (pH=3.70)	6.66×10 ⁻⁴	0.8604	1.321	0.9887	3	13	3.2	50
	360 (pH=3.45)	2.14×10 ⁻⁴	0.6744	1.241	0.9976	2	12	1.9	42
Adjust pH by adding HCl	pH=4.09	9.66×10 ⁻⁴	0.7608	1.787	0.9976	8	22	4.4	61
	pH=3.99	9.36×10 ⁻⁴	0.7936	1.793	0.9932	7	19	4.0	60
	pH=3.70	9.24×10 ⁻⁴	0.7788	1.853	0.9941	6	18	3.9	58
	pH=3.45	7.71×10 ⁻⁴	0.7704	1.762	0.9872	6	16	3.8	55

HCl without Ac-, Rat and L decreased indistinctively. These results imply that HAc mostly affect the formation/adsorption processes of intermediates, and run to form more soluble corrosion product¹⁷⁾, on the other hand, H⁺ has no distinct contribution to the formation/adsorption processes of intermediates. However, there was consistent in the characteristics of EIS measured in the CO₂-saturated solution with and without Ac-, this implied that acetic acid and acetate accelerated corrosion of N80 steel, but did not change the mechanism of the anodic processes.

4. Conclusions

1. HAc is as catalyst in CO₂ corrosion. As a result, the corrosion rate is accelerated in the presence of acetate ion even pH value of solution increased.
2. Because adsorbed HAc can be directly reduced on the surface of electrode, the cathodic reduction process was enhanced.
3. Ac- plays an important role in anodic dissolution processes, which mainly affects the formation /adsorption of intermediates.

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