



Influence of temperature and thiosulfate on the corrosion behavior of steel in chloride solutions saturated in CO₂

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ABSTRACT

The corrosion resistance of mild steel in environments of 1 M NaCl solutions saturated in CO₂ was investigated in the absence and presence of different concentrations of thiosulfate (0.01–1 M Na₂S₂O₃), one of the main sulfide oxidation product, at 22 and 50 °C. Polarization measurements and immersion tests revealed remarkable increase in the chloride corrosion rate in the presence of dissolved CO₂ species and/or thiosulfate ions. Solutions containing Cl⁻-S₂O₃²⁻-dissolved CO₂ species exhibited higher corrosion attack than those conducted in Cl⁻-S₂O₃²⁻ or Cl⁻-dissolved CO₂ solutions and is increased with increasing thiosulfate concentration. The room temperature results were compared to those measured at 50 °C. Similar polarization type behavior was obtained with higher corrosion rates for the higher solution temperature. Although the presence of thiosulfate and/or dissolved CO₂ species activated the steel anodic/cathodic polarization curves in chloride solutions, this effect was more pronounced on the cathodic side and in the presence of dissolved CO₂ species. The cathodic current density showed substantial displacement to more active values in the presence of thiosulfate and/or dissolved CO₂ and increased with increasing thiosulfate concentration.

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1. Introduction

Carbon dioxide dissolved in water or aqueous solutions has been known to cause corrosion damage to a variety of steel technical equipment in oil and gas production industries [1–4]. In oil industry, CO₂ corrosion results from the water saturated with CO₂ containing chloride associated with the crude/gas production. In the last two decades the CO₂ corrosion has gained a very serious concern with the use of enhanced oil recovery techniques based on CO₂ injection reservoirs and sweet gas production from deeper wells [5–7].

When dissolved in water, CO₂ is hydrated to give carbonic acid, which is corrosive to steel. Its aggressiveness depends on pH, oxygen content, temperature, CO₂ partial pressure and solution chemistry beyond alloy composition and hydrodynamic of the system [7–14]. In general, CO₂ increases steel uniform corrosion rate with increasing CO₂ partial pressure [8–12], solution velocity [13,14], or with the presence of acetic acid [15,16]. The increase in solution pH usually leads to a considerable decrease in corrosion rate [9–12]. Higher oxygen concentration contributes to an increase in the rate of the cathodic reaction (oxygen reduction), thus increasing corrosion rate [17–19]. The presence of Cr in the steel matrix is useful to suppress localized attack [20] and diminish the uniform corrosion

rate and is more pronounced at low pH medium [21,22]. At low temperature (i.e. less than 60 °C) the CO₂ corrosion increases with temperature and the scale formed on steel surface (iron carbonate) are regarded as non protective. At higher temperature, however, protective films are formed more easily and the corrosion rate goes through a maximum. This scaling temperature depends on flow rate and CO₂ pressure, among other factors [8–11,17]. CO₂ corrosion in general is controlled by addition of inhibitors with concentrations depending on the corrosion rate [1,2] or by using more resistant material such as stainless steel alloys [17,23].

The so-called CO₂ corrosion usually occurs in the absence of oxygen. Under appropriate kinetic conditions a FeCO₃ protective film can be formed at the metal surface. The protectiveness of the surface film depends on the nature of the base alloy (composition, heat treatment) and the environment (temperature, CO₂ partial pressure, pH) [7,11,13,19,24,25]. In presence of O₂, however, this film is unstable and easily transformed to iron oxide [19,24,25].

The presence of H₂S can often enhance sweet corrosion and produce more corrosive environment than would occur by either species separately. H₂S is known to form iron sulfide (FeS) with different crystalline structure. This film is cathodic to steel and, therefore, provides a galvanic driving force for localized attack at exposed patches of steel or pores in the film. The composition of FeS scale depends on the H₂S partial pressure and become more adherent with higher corrosion rate at higher H₂S partial pressure [26–28].

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In field applications, oxygen may enter production equipment due to water or inhibitor injection [12,24]. Stratal water extracted along with oil has been found to contain dissolved impurities like H₂S, CO₂, gaseous hydrocarbons and atmospheric oxygen [28]. When water containing H₂S mixes with oxygenated water the hydrogen sulfide can be oxidized by O₂ resulting in the formation of several reduced species, such as thiosulfate, sulfite, elemental sulfur and polysulfide as well as sulfate [29–31]. Most of the literature are dealt with the corrosion of steel alloys in chloride solutions containing CO₂-sulfide species. Thus the main objective of this paper was to investigate the effect of thiosulfate, one of the main sulfide oxidation product, on the corrosion behavior of steel in NaCl solutions saturated in CO₂. Thiosulfate (S₂O₃²⁻) is known to be aggressive to high alloyed steels in chloride containing solutions and is responsible for the corrosion of steel alloys in environments related to petroleum industry [32–34]. The intensity of thiosulfate corrosion is further enhanced by the presence of CO₂ species [35]. The aggressiveness of thiosulfate is attributed to its ability to catalyze the anodic dissolution of the steel through the formation of metal sulfide on the alloy surface [36,37].

2. Experimental

The specimens used in this study were made of steel with the following chemical composition; C: 0.1, Mn: 0.05, S 0.05, P: 0.04, Fe: bal. Steel specimens with a thickness of approximately 3 mm were cut from steel sheet. For polarization measurements, each specimen was connected with electrical wire and covered with epoxy resin allowing a surface area of about 2 cm² to be exposed to the solution medium. Prior to a polarization test, the specimens were prepared by wet grinding with silicon carbide papers ranging from 600 to 1000 grit, washed with distilled water and dried with cold air.

The corrosion cell used in this study was made of 500 ml well sealed glass bottle containing 400 ml of test solution with the three electrode system; saturated calomel electrode, platinum auxiliary electrode and test electrode. These electrodes were placed directly in the test solution. The corrosion cell was connected to a Wenking potentiostat/galvanostat POS 2.

Prior to CO₂ experiments, the steel electrode was held above the solution level and the test solution was purged with CO₂ gas (at atmospheric pressure) for 60 min before the steel electrode was immersed into the solution. The solution pH was found to change during the first five minutes before reaching to final saturation value. The final pH values of these solutions at room temperature are listed in Table 1. The solution temperature was controlled using a water bath.

Repeated linear polarization resistance measurements (LPR) were carried out by anodically sweeping the potential 10 mV below the open circuit potential to 10 mV over this potential at a rate of 12 mV/min. The anodic or cathodic potentiodynamic polarization curves were then conducted by sweeping a fresh steel sample 200 mV from the free corrosion potential in the anodic or cathodic

direction respectively with a scanning rate of 12 mV/min. The corrosion current was then calculated by means of the LPR and by the analysis of the potentiodynamic polarization curves using the following formula

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

where R_p is the polarization resistance ($\Omega \text{ cm}^2$), β_a and β_c is anodic and cathodic Tafel constants respectively (V decade^{-1}) and i_{corr} is corrosion current density (A cm^{-2}). In this work it was found that the values of β_a and β_c in plain chloride solutions at 22 °C were 70 and 210 mV/dec respectively. At 50 °C, however, these values in respective order were 54 and 180 mV/dec. In presence of dissolved CO₂ and S₂O₃²⁻ the value of β_c was very large, i.e. $\beta_c \gg \beta_a$ and the above equation reduces to the simplified equation

$$i_{corr} = \frac{B}{R_p} = \frac{\beta_a}{2.303 R_p} \quad (2)$$

The penetration rates (in mpy) was finally calculated using Faraday's law:

$$\text{Corrosion rate (mpy)} = \frac{Z \times i \times t \times 393.7}{nF\rho} \quad (3)$$

where Z is average atomic weight (55.8 g mol⁻¹), n is number of electrons (2 electrons), F is Faraday's constant (96,500 A s mol⁻¹), t is time (s) (31,536,000 s yr⁻¹), i is current density (A cm^{-2}), ρ is density of steel (7.86 g cm⁻³)

Mass loss measurements were also conducted to study the steel corrosion behavior in the chloride/thiosulfate/dissolved CO₂ (sat.) solutions at 22 ± 2 °C. The test cells were made of 500 ml well sealed glass bottles containing 400 ml of test solution with two pre-weighted steel coupons in each bottle. Prior to immersion the coupons (approximately 6.5 cm² surface area) were polished with emery papers 600 and 1000 mesh, cleaned with distilled water degreased in acetone and weighted using four decimal digital balance. Test solutions containing dissolved CO₂ was prepared by purging CO₂ gas for 1 h. During the CO₂ bubbling the coupons were held above the solution level. The removed coupons after 14, 28 or 50 days were dried and the corrosion product were scrapped off by a metal brush. The coupons were then washed by distilled water, dipped in nitric acid, washed thoroughly by distilled water, dried by cold air and finally weighed. The weight loss was expressed in terms of mpy. It should be mentioned that all tests conducted in this study were carried out at stagnant conditions.

3. Results and discussion

The effect of CO₂ and/or different concentrations of thiosulfate on steel corrosion behavior was examined by conducting the experiments in 1 M NaCl solutions under two techniques: (1) LPR and polarization tests at 22 and 50 °C and (2) weight loss method at 22 °C.

3.1. Polarization measurement

Fig. 1 summarizes the value of steel corrosion rates obtained from the polarization curves and LPR (Table 2) in 1 M NaCl solutions with and without CO₂ and in the absence and presence of various concentrations of thiosulfate (0.01–1 M Na₂S₂O₃) at 22 and 50 °C. As seen in this figure chlorides solutions containing both S₂O₃²⁻ and CO₂ species had the highest corrosion rate (most aggressive solutions). This was followed by chloride-thiosulfate solutions. Although the presence of CO₂ has markedly increased the chloride corrosion rate of steel by about 1.7 times, chloride solutions under

Table 1
pH of experimental solutions used in this work

No.	Solution	pH
1	1 M NaCl	6.8
2	1 M NaCl + CO ₂ (sat.)	3.33
3	1 M NaCl + 0.01 M Na ₂ S ₂ O ₃	6.53
4	1 M NaCl + 0.1 M Na ₂ S ₂ O ₃	6.7
5	1 M NaCl + 1.0 M Na ₂ S ₂ O ₃	6.85
6	1 M NaCl + 0.01 M Na ₂ S ₂ O ₃ + CO ₂ (sat.)	3.92
7	1 M NaCl + 0.1 M Na ₂ S ₂ O ₃ + CO ₂ (sat.)	4.02
8	1 M NaCl + 1.0 M Na ₂ S ₂ O ₃ + CO ₂ (sat.)	4.35

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