Influence of H$_2$S Partial Pressure on the Corrosion Behavior of X60 Carbon Steel

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Abstract

The objective of this paper is to study the influence of H$_2$S/CO$_2$ partial pressure ratios on the corrosion behavior of carbon steel X60. In this work, micromorphology of corrosion product was investigated by X-ray diffraction and scanning electron microscopy. The corrosion behavior of X60 steel under different conditions was analyzed. The results showed that the presence of H$_2$S induced the formation of iron sulfide films that provide protective properties to the metal and the corrosion rate decreased with increasing the H$_2$S/CO$_2$ partial pressure ratios. This behavior is because of the increase in the corrosion film thickness with increasing the H$_2$S/CO$_2$ partial pressure ratios.

Keywords: Sour corrosion; H$_2$S/CO$_2$ partial pressure ratios; Carbon steel; Electrochemical techniques

Introduction

Sour corrosion is the most common corrosion in oil and gas industry and apart from inducing severe general and localized corrosion, the presence of H$_2$S could cause hydrogen induced cracking (HIC) and sulfide stress corrosion cracking (SSCC) of pipelines and tubings [1-4]. Even though corrosion resistant alloys (CRA) has long been available as a material selection option that mitigates CO$_2$ and H$_2$S corrosion, carbon steel is in general more cost-effective for oil and gas facilities and hence, is the most widely used material option. Over the past years, number of researchers have studied the effect of hydrogen sulfide gas concentrations on the corrosion behavior of carbon steel [5-7]. Several studies have shown that the presence of H$_2$S could either cause an acceleration or an inhibition of the corrosion of carbon steel, depending on the partial pressure of H$_2$S [8]. Some studies also demonstrated the mechanism of H$_2$S/CO$_2$ corrosion of pipeline and presented certain models [9-12]. Though H$_2$S/CO$_2$ corrosion of pipelines has been studied widely, most of the studies focused on the characteristics of corrosion products and weight loss test after immersion. The corrosion mechanism of steel under H$_2$S/CO$_2$ conditions remains poor, especially in the environments with high H$_2$S partial pressure. In addition, no clear description is available on the effects of different H$_2$S/CO$_2$ partial pressure ratios on the corrosion mechanism of pipeline steel. The objective of this study is to evaluate the effect of H$_2$S/CO$_2$ partial pressure ratios on corrosion of carbon steel in NACE solution A, and to characterize the corrosion products film.

Experimental Procedure

Corrosion tests were conducted on carbon steel 5LX60 and the sample surface was grounded to a 600-grit silicon carbide (SiC) finish. The sample was cleaned using detergent and warm water, followed ultrasonically by acetone, after which it was dried thoroughly. NACE solution A (5wt% NaCl and 0.5wt% acetic acid) was used in this work and corrosion tests were conducted at room temperature. The total H$_2$S/CO$_2$ partial pressure was maintained at 4.0MPa. The amounts of H$_2$S and CO$_2$ were adjusted to obtain the environments with different H$_2$S/CO$_2$ partial pressure ratios (0.01:0.99, 0.1:0.9 and 1:0) which were labeled in the figures as 1% H$_2$S, 10% H$_2$S and 100 H$_2$S, respectively. The blended gas was continuously purging in the corrosion cell during the exposure time at constant rate (25ml/min). Potentiodynamic scan were utilized in-situ to measure polarization resistance and corrosion current density of produced films. The test electrode was allowed to stabilize for approximately 60min.
Immediately following the stabilization period, the test electrode was polarized at a scan rate of 1.66mV/s from an initial potential of -1V (vs. OCP) to the final potential of +1V. Phase composition analysis of the corrosion film was identified by X-ray diffraction (XRD) technique utilizing a PANalytical X’Pert PRO instrument operated at 45kV and 40mA with Cu kα radiation (λ=1.5418Å). Scanning electron microscope (SEM) was employed to analysis morphology of corroded samples.

**Result and Discussion**

The corrosion behavior of carbon steel exposed to the H₂S/CO₂ environments is influenced by the structural characteristics of the corrosion products. After 96hrs of exposure, corrosion products covered the entire coupon surface. Figure 1 shows the SEM surface morphologies of the coupons exposed at different H₂S/CO₂ partial pressure ratios where flower-like corrosion products were observed on the surface of two coupons exposed to 1% H₂S and 10% H₂S but with larger size in sample exposed 10% H₂S. In contrast with coupons exposed to 100% H₂S, flake-like corrosion products were seen clearly on the surface. The XRD pattern in Figure 2 confirms presence of mackinawite as main corrosion product and decreases with decreasing partial pressure of H₂S. The corrosion behavior of carbon steel exposed to different H₂S content in NACE solution A was evaluated through the potentiodynamic polarization technique as shown in Figure 3. The polarization curves show that the corrosion behavior of formed corrosion products films is small differences but significant. The potentiodynamic polarization measurements confirm the inhibition effect of H₂S on corrosion of carbon steel in the NACE solution A.

![Figure 1](image1.png)

**Figure 1:** SEM images on the surface morphologies of the coupons exposed to
a) 1% H₂S
b) 10% H₂S and
c) 100% H₂S balanced with CO₂ in NACE solution A at room temperature.

![Figure 2](image2.png)

**Figure 2:** XRD pattern on the surface of the coupons exposed to different H₂S/CO₂ partial pressure ratios in NACE solution A at room temperature.
After one day of immersion, the anodic and cathodic polarization curves are exactly same trend for both H$_2$S concentrations 10 and 100 mole%. Whilst for 1% H$_2$S concentration, it is found that the corrosion potential of X60 was slightly higher than that obtained from other H$_2$S/CO$_2$ partial pressure ratios. The polarization resistance of X60 coupon exposed to 10 and 100% H$_2$S decreases with increasing immersion time. Whilst, the polarization resistance measured on the coupon exposed to 1% H$_2$S increased sharply until reach 24hrs of exposure then decreased suddenly with the rest of immersion time. In addition, the current densities of coupons exposed to 10% H$_2$S, 100% H$_2$S increased rapidly during first day of immersion by more than two times compared to the one exposed to 1% H$_2$S. It can be remarked clearly that the corrosion rate of coupon exposed to 100% H$_2$S was very high compared to other H$_2$S/CO$_2$ partial pressure ratios. XRD composition analysis for coupon exposed to 100% H$_2$S was almost 100% mackinawite phase presence in the formed corrosion film. This can be the driving force of the observed aggressive corrosion behavior. It was reported [8] that the significant impact of precipitated mackinawite phase of iron sulphide can have in the acceleration of the localized attack.

**Conclusion**

In this study, the difference in corrosion behavior of carbon steel exposed to three different H$_2$S/CO$_2$ partial pressure ratios in NACE solution A was compared by characterizing corrosion products and analyzing electrochemical measurements. The experimental results demonstrated that the corrosion rate decreased with increasing the H$_2$S/CO$_2$ partial pressure ratios. However, in case of damage in corrosion films, the experimental results showed inversely where the corrosion rate increased with increasing the H$_2$S/CO$_2$ partial pressure ratios. The mackinawite is the most aggressive component of iron sulphide phase and it became more superiority in the corrosion products with increasing the H$_2$S/CO$_2$ partial pressure ratios.

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