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Corrosion Investigation of Pipeline Steel in Hydrogen Sulfide Containing Solutions

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Abstract: The hydrogen-induced cracking (HIC) behavior of X70 pipeline steel was studied by means of Linear Polarization Resistance (LPR), hydrogen permeation tests, weight loss and Scanning Electron Microscopy (SEM). In this study, the dissolved H₂S was created by chemical reactions in solution. The specimens were immersed into synthetic sea water saturated with H₂S. The experimental results showed that the increase of exposure time and H₂S concentration leads to an increase of the hydrogen content in X70 steel, which plays a key role in the initiation and propagation of HIC.

Key words: Hydrogen sulfide, hydrogen induced cracking, polarization, sour environment, X70 steel

INTRODUCTION

Several scientific articles have been discussed about Hydrogen Induced Cracking (HIC) of carbon steel pipe (Venegas *et al.*, 2005; Kittel *et al.*, 2008; Asmara and Ismail, 2011). Numerous researchers approved a correlation between HIC and hydrogen concentration (C_0). HIC will happen when hydrogen concentration (C_0) on metal surfaces exceeds the threshold hydrogen concentration (C_{th}). C_{th} will increase when material strength increase. C_0 depend on different parameter such as H₂S partial pressure, pH and composition while C_{th} is known to be dependent on separation and inclusions in the matrix (Elboujdaini *et al.*, 2003; Shehata *et al.*, 2008).

So far, a lot of work has been done to investigate the corrosion phenomena such as HIC and SCC of X70 pipeline steel. Dong *et al.* (2009) explained oxide and oxysulfide inclusions in X70 steel are more unfavorable than nitride inclusions in HIC. They found that the hydrogen trap density estimated at room temperature is pretty high that can lead to X70 steel become sensitive to HIC. Arzola *et al.* (2006) reported the corrosion behavior of X70 pipeline steel exposed in several H₂S-containing solutions that indicated the presence of H₂S in a NaCl solution decreased the impedance of steel, compared to a

NaCl solution free of H₂S. They also showed corrosion rate values increased in turbulent flow conditions.

The influence of different H₂S concentration on Hydrogen induced cracking in X70 pipeline steel under various temperatures were investigated in this work.

MATERIALS AND METHODS

The specimens used in this study were made of X70 pipeline steel with elemental composition as shown in Table 1. The X70 specimen was connected to copper wire and covered with epoxy resin with an exposed area of 1 cm². The specimens were polished up to 800 grit silicon

Table 1: Elemental composition of X70 steel

Elements	Chemical composition (wt.%)
C	0.080
Si	0.290
Mn	1.590
P	0.013
S	0.002
Cu	0.080
Ni	0.100
Cr	0.020
Mo	0.110
V	0.047
Al	0.023
Nb	0.034
Ti	0.016

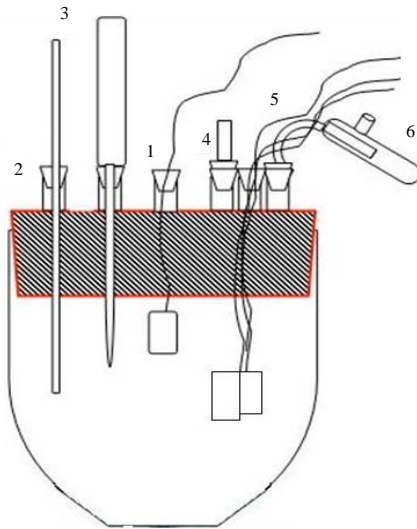


Fig. 1: Schematic representation of the experimental test cell: 1: Platinum counter electrode, 2: Temperature probe, 3: Reference electrode, 4: Chemical inlet, 5: Sample holder (working electrode) 6: Gas outlet, 4: Luggin capillary

Table 2: Different concentration of chemicals for test matrix

Material	Concentration of solution (mol L ⁻¹)			
	C1	C2	C3	C4
Na ₂ S.9H ₂ O	0.015	0.035	0.055	0.075
CH ₃ COOH	0.035	0.082	0.128	0.175

carbide paper, rinsed with deionised water and degreased in acetone. Experiments were conducted at atmospheric pressure in a glass cell (Fig. 1). A typical three-electrode setup was used with a Saturated Calomel Electrode (SCE) as the reference electrode, a platinum counter electrode and X70 steel specimens as the working electrodes.

Corrosion rates (CR) in weight loss experiment were measured by using following Eq. 7:

$$CR = \frac{534\Delta W}{DAT} \quad (1)$$

where, CR is corrosion rate (mpy), ΔW is the weight loss (mg), D is specimen density (g cm⁻³), A is specimen exposure surface (in²) and T is exposure time (h).

Na₂S.9H₂O was chosen as test material to replace H₂S because of the toxicity of H₂S. Brain solution was 3% NaCl solution. Different concentrations of H₂S containing solution were made as shown in Table 2.

RESULTS AND DISCUSSION

The potentiodynamic polarization curves for X70 carbon steel in solutions containing different H₂S concentration at 25 and 50°C are shown in Fig. 2 and 3. As it can be seen cathodic curve (hydrogen evolution reaction) was accelerated by increasing H₂S concentration while anodic curves showed similar current densities. This anodic curve is related to dissolution of iron.

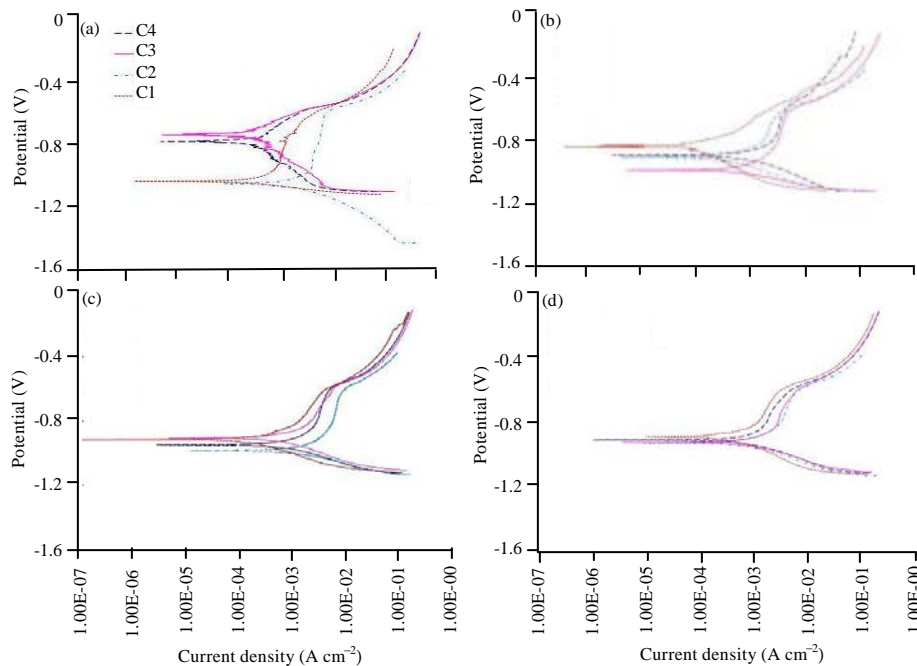


Fig. 2(a-d): Cyclic polarization curves of X70 carbon steel sample in 3% NaCl solution containing different H₂S concentration (C1, C2, C3 and C4) in different exposure times (a) 24, (b) 48, (c) 72 and (d) 96 h at 25°C

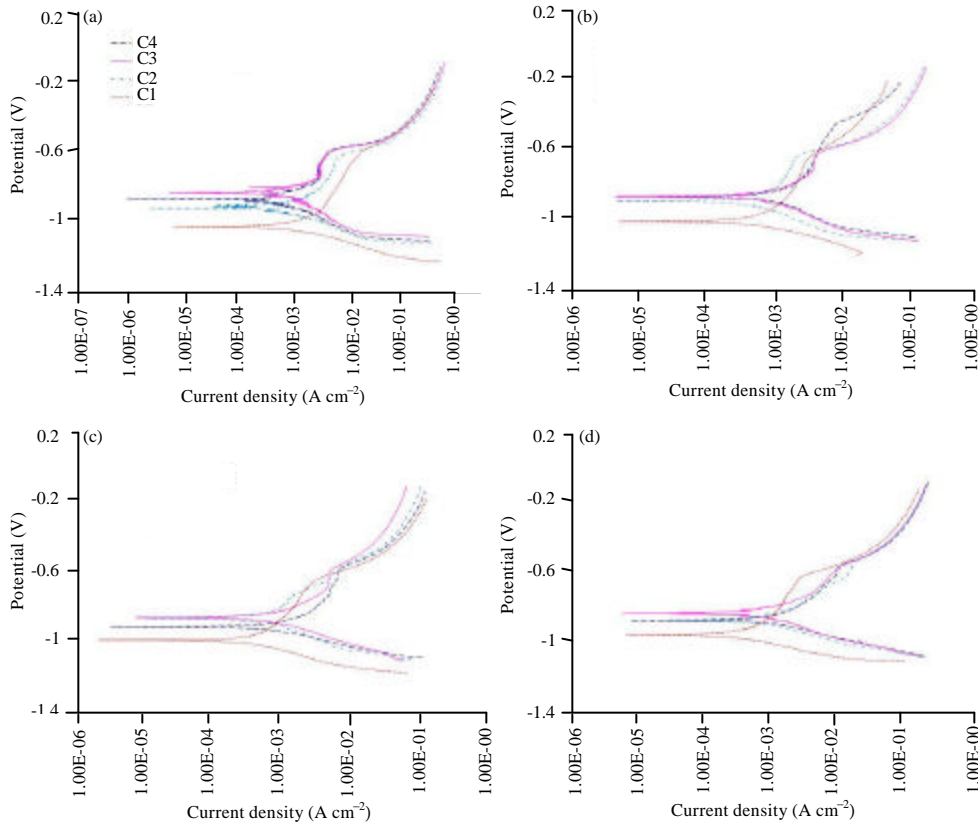


Fig. 3(a-d): Cyclic polarization curves of X70 carbon steel sample in 3% NaCl solution containing different H₂S concentration (C1, C2, C3 and C4) in different exposure times, (a) 24, (b) 48, (c) 72 and (d) 96 h at 50°C

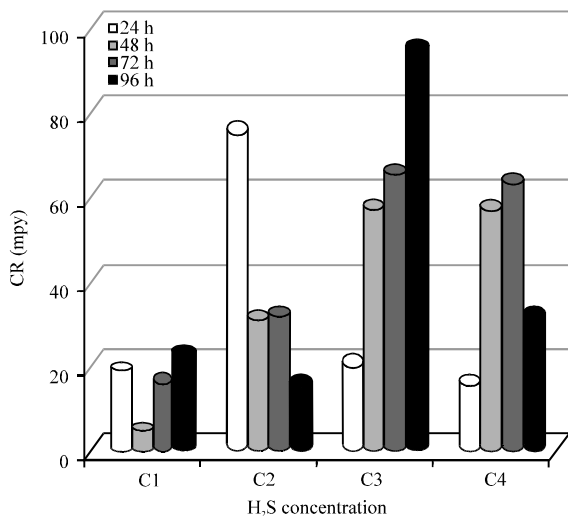


Fig. 4: The 3D column chart of corrosion rate vs. different H₂S concentration (C1, C2, C3 and C4) in different exposure time at 25°C

The change in corrosion values can be explained by growth mechanisms of iron sulfide film. Iron sulfide layer has a thickness limitation. When film grows to critical

values, it will be break up. So, when the corrosion rates are minimum, the iron sulfide thickness is the best values and electrons and ferrous ions will transfer through the iron sulfide film.

The mechanism of the effect of hydrogen sulfide on carbon steel is defined by the formation of hydrogen atoms that caused the formation of a molecular surface complex (Fe H-S-H) which is cathodic polarization. Then, some of the hydrogen atoms will diffuse, whereas, other may recombine (Elboujdaimi *et al.*, 2003):

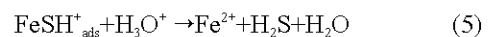
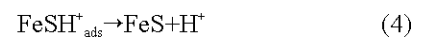
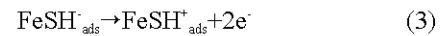


Figure 4 and 5 show corrosion rate in different H₂S concentration. Changes in corrosion rate are due to iron sulfide film role in surface passivation. Whenever, this protective layer detaches from surface, corrosion rate will increase. A cover of the black corrosion film was detected

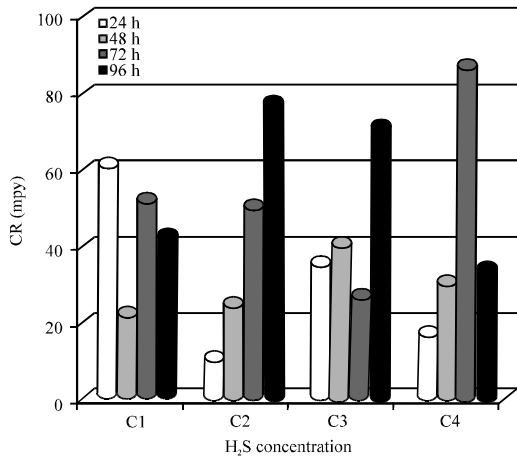


Fig. 5: 3D column chart of corrosion rate vs. different H₂S concentration (C1, C2, C3 and C4) in different exposure time at 50°C

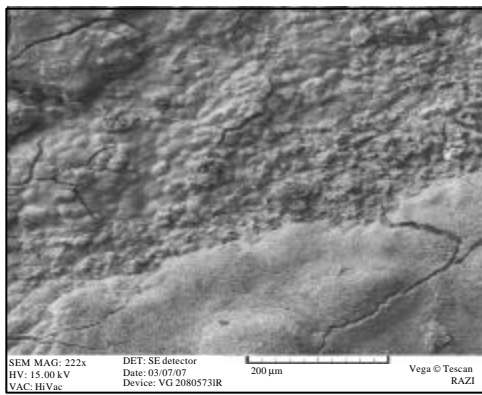


Fig. 6: SEM image of corrosion product on sample surface

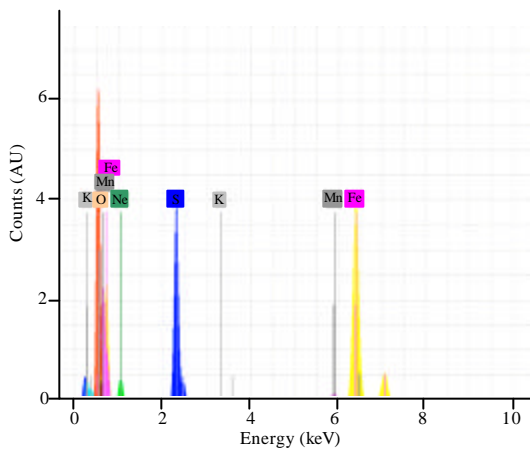


Fig. 7: EDX analysis of corrosion product

on all specimen's surfaces after exposure in the test solution. Figure 6 illustrates an SEM image specimen after

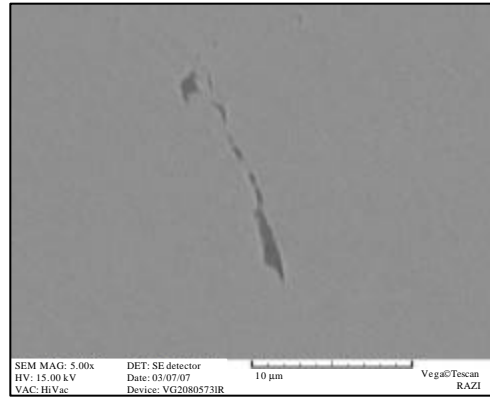


Fig. 8: SEM image of HIC on sample surface

Table 3: Permeable hydrogen concentration

API 5L X70		
Temp.	H ₂ conc. (mL)	H ₂ S conc.
25°C	0.5	C1
	0.3	C2
	0.3	C3
	0.3	C4
50°C	0.8	C1
	0.6	C2
	1.0	C3
	0.8	C4

exposure 96 h in 25°C in sour environment. Cracks in the FeS film show that this layer is not a stable layer for surface passivation and it cannot protect steel surface from further corrosion.

According to Fig. 7, EDX analysis shows high sulfur content in corrosion product that is due to FeS film in sample surface.

Figure 8 shows an SEM image of sample surface exposure 96 h in 25°C in sour environment. HIC is clear in this image.

Table 3 shows the permeable hydrogen concentration. It can be considered as amount of hydrogen that penetrate into the steel and cause HIC. In first step hydrogen attaches the steel by adsorption onto the water to steel interface and then by being absorbed into the steel as hydrogen. The amount of hydrogen penetration depends on the corrosion rate of the steel surface and the concentration of anions such as HS⁻ that reduce the tendency to produce hydrogen gas and promotes the hydrogen (H₂) to enter the steel (Tung *et al.*, 2001). By increasing the temperature, hydrogen concentration increases.

CONCLUSION

Very thin sulfide film, possibly mackinawite, was formed rapidly on the steel electrode in all experiments with different concentration of H₂S.

By increasing the temperature, hydrogen concentration increased. So, corrosion rate increased. HIC was detected in sample surfaces after hydrogen penetration.

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