Quantitative Study of the Hydrogen Entry Behavior of Low Alloy Steels for Various Sour Environments

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Hydrogen entry behavior was investigated with different H$_2$S partial pressures over pH 5.0 and was quantified for various sour environments using American Petroleum Institute grade X65 line pipe and line pipe plate. Hydrogen permeability dramatically decreased for H$_2$S partial pressures of 0.1 MPa exceeding pH 5.5 and 0.01 MPa exceeding pH 6.2. This is caused by the formation of a stable iron sulfide film. On the other hand, hydrogen permeability proportionally decreased with increasing pH for H$_2$S partial pressure of 0.001 MPa up to pH 6.0. The critical pH at which iron sulfide becomes quite stable was predicted from the equation of the relation among pH, H$_2$S partial pressure, and iron ion activity based on potential vs. pH in Fe–S–H$_2$O. Hydrogen concentration into steel invading from various sour environments was proposed and quantified.

KEY WORDS: hydrogen; sour environment; carbon steel; low alloy steel; hydrogen permeation.

1. Introduction

Sulfide stress cracking (SSC) and hydrogen-induced cracking (HIC) often occur in wet H$_2$S environments (sour environment) wherein the pH becomes less than 5.0 because hydrogen enters into the internal surface of oil country tubular goods (OCTGs) or line pipes by corrosion. Sour resistant OCTG or line pipes have been developed to prevent SSC and HIC.1–5) For example, NACE TM0177 solution B,6) which comprises 5% sodium chloride and 0.4% sodium acetate with an initial pH of 3.5 is requested for SSC tests. On the other hand, NACE TM0284 solutionA,7) which comprises 5% sodium chloride and 0.5% acetic acid with an initial pH of 2.7 is requested for HIC tests. However, various H$_2$S partial pressure and various pH exist in actual oil and gas wells around a world. Therefore, SSC and HIC tests are often required for solutions with H$_2$S partial pressure exceeding 5.0 and to quantify hydrogen concentration into steel for sour environments using American Petroleum Institute (API) grade X65 line pipe and line pipe plate.

2. Experimental Procedure

2.1. Test Material

The chemical composition of the steels tested is indicated in Table 1. These steels were used for plate of line pipes and line pipe of API grade X65. Hydrogen entry behavior was investigated using these steels. Slabs were melted in a 300 ton LD converter and hot rolled into 20 mm thickness plates in Thermo-Mechanical Control Process. The specimens subjected to the hydrogen permeation method were taken from quarter portion of the plate and pipe. These specimens with 20 mm in length, 50 mm in width, and 1 mm in thickness were cut, machined, and electro-polished.

2.2. Hydrogen Permeation Test

Hydrogen permeation test was performed to measure the hydrogen concentration in steel. Figure 1 shows the apparatus of the hydrogen permeation test. The specimen was immersed in the left-side cell, in which a corrosive solution saturated with H$_2$S was poured. The current detected by the oxidation of hydrogen was measured in the right-side cell filled with 1 mol/L NaOH solution. Ni plating was applied to the specimen surface facing the right-hand side.14,15) The hydrogen concentration in steel was expressed by hydrogen permeability (Per). Per is defined in Eq. (1).

\[ \text{Per} = J \times L, \]

where \( J \) refers to the measured current density and \( L \) refers to the thickness of the test specimen. Hydrogen permeabil-
ity is the parameter that is independent of material factors such as diffusion coefficient. Two kinds of test solutions were made. One solution consisted of 1 mol/L acetic acid containing 5 mass% sodium chloride. The other solution consisted of 1 mol/L acetic sodium acetate containing 5 mass% sodium chloride. These solutions were mixed in order to adjust pH. The dissolved oxygen was minimized by deaerating in nitrogen gas before introducing H$_2$S gas. Then, H$_2$S gas was introduced to the solution continuously. Here, H$_2$S gas was introduced after permeability was lowered to $0.05 \times 10^{-4}$ A/m. The pH was changed from 5.0 to 6.2. The H$_2$S partial pressure was changed from 0.1 to 0.001 MPa. The test temperature was maintained at 25°C and the test duration was 96 h.

3. Results

3.1. Effect of H$_2$S Partial Pressure on Hydrogen Entry into Steel Above pH 5.0

The effect of H$_2$S partial pressure on hydrogen entry into steel was investigated for steel B in weak acid above pH 5.0. The hydrogen permeability for H$_2$S partial pressures of 0.1, 0.01, and 0.001 MPa and at pH of 5.0 and 6.0 was indicated from Figs. 2 to 4. Hydrogen permeability was used as the parameter for hydrogen concentration into steel. In the case of H$_2$S partial pressure of 0.1 MPa at pH 5.0, the hydrogen permeability reached $3.2 \times 10^{-4}$ A/m and indicate maximum value immediately after the test started and then indicated the same value for 96 h. On the other hand, in the case of H$_2$S partial pressure of 0.1 MPa at pH 6.0, the hydrogen permeability dramatically decreased to $0.1 \times 10^{-4}$ A/m immediately after the test started and reached $1.0 \times 10^{-4}$ A/m and indicated maximum value in Fig. 2. In the case of H$_2$S partial pressure of 0.01 MPa at pH of 5.0 and 6.0, the hydrogen permeability reached $1.5 \times 10^{-4}$ and $1.0 \times 10^{-4}$ A/m in maximum immediately after the test started and then indicated the same value for 96 h in Fig. 3. In the case of H$_2$S partial pressure of 0.001 MPa at pH of 5.0 and 6.0, the hydrogen permeability reached $1.0 \times 10^{-4}$ and $0.8 \times 10^{-4}$ A/m in maximum immediately after the test started and then
indicated the same value for 96 h in Fig. 4. Here hydrogen permeability drastically decreased for the H$_2$S partial pressure of 0.1 MPa at pH 6.0 because this phenomenon was not observed in others condition. The dramatic decrease in the hydrogen permeability is considered to be caused by the formation of iron sulfide, which becomes quite stable over pH of 5.0 in the potential vs. pH diagram.$^{16,17)}$ This phenomenon is discussed later in detail.

Therefore, the critical pH at which the hydrogen permeability starts to decrease was measured for H$_2$S partial pressure of 0.1, 0.01, and 0.001 MPa. In the case of H$_2$S partial pressure of 0.1 MPa, hydrogen permeability did not decrease up to pH 5.3; however, it dramatically decreased at pH 5.5 in Fig. 5. The critical pH was determined to be 5.4 for H$_2$S partial pressure of 0.1 MPa. Similarly, in the case of H$_2$S partial pressure of 0.01 MPa, hydrogen permeability did not decrease up to pH 6.0; however, it dramatically decreased at pH 6.2 in Fig. 6. The critical pH was determined to be 6.1 for H$_2$S partial pressure of 0.01 MPa. Here, it seems that hydrogen permeability was still kept at $0.2 \times 10^{-4}$ A/m. Therefore, this is future subject why hydrogen permeability decreased less than $0.05 \times 10^{-4}$ A/m in this condition although FeS film is formed because hydrogen permeability drastically decreases after it reaches maximum value of $0.6 \times 10^{-5}$ A/m. On the other hand, in the case of H$_2$S partial pressure of 0.001 MPa, hydrogen permeability did not decrease up to pH 6.0 as indicated in Fig. 4.

4. Discussion

4.1. Effect of H$_2$S Partial Pressure on Critical pH

As mentioned before, hydrogen permeability drastically decreased because of the formation of iron sulfide, which becomes quite stable over the critical pH. The critical pH for the H$_2$S partial pressures of 0.01 and 0.001 MPa was calculated using the potential vs. pH diagram.$^{17)}$ The critical pH line at which the iron sulfide becomes stable from potential vs. pH diagram indicated in arrow of Fig. 7 is determined by the solubility of FeS.

$$\text{FeS} - \text{Fe}^{2+} + \text{H}_2\text{S} + 2 \text{H}^+ = 0 \quad (2)$$

The equilibrium constant for the dissolution of FeS is $\log K = -3.7$. Depending on pH, the equilibrium may change at different Fe$^{2+}$ activities according to

$$\log a_{\text{Fe}^{2+}} = 3.7 - 2 \text{pH} - \log P_{\text{H}_2\text{S}} \quad (3)$$

where $a_{\text{Fe}^{2+}}$ is the iron ion activity (mol/L) and $P_{\text{H}_2\text{S}}$ is the H$_2$S partial pressure (atm).

$$\log a_{\text{Fe}^{2+}} = 2.7 - 2 \text{pH} - \log P_{\text{H}_2\text{S}} \quad (4)$$

where $a_{\text{Fe}^{2+}}$ is the iron ion activity (mol/L) and $P_{\text{H}_2\text{S}}$ is the H$_2$S partial pressure (MPa). If the pressure of H$_2$S is equal to 1 atm (0.1 MPa), the above formula may be simplified.

$$\log a_{\text{Fe}^{2+}} = 3.7 - 2 \text{pH} \quad (5)$$

Here, the perpendicular lines 0, −2, −4, −6 correspond to $a_{\text{Fe}^{2+}}$ of 1.0, $10^{-2}$, $10^{-4}$, $10^{-6}$ mol/L in Fig. 7. First, the iron ion activity was calculated to be $1.0 \times 10^{-7}$ mol/L using

![Fig. 5](image1.png)

**Fig. 5.** Hydrogen permeation behavior with time in pH 5.0, 5.3, and 5.5 at H$_2$S partial pressure of 0.1 MPa in steel B.

![Fig. 6](image2.png)

**Fig. 6.** Hydrogen permeation behavior with time in pH 5.0, 6.0, and 6.2 at H$_2$S partial pressure of 0.01 MPa in steel B.

![Fig. 7](image3.png)

**Fig. 7.** Potential vs. pH diagram for Fe–S–H$_2$O.
Eq. (4) because the critical pH for H$_2$S partial pressure of 0.1 MPa was determined to be 5.4 from Fig. 5. The relation between hydrogen permeability and corrosion current density was expressed in Eq. (6).

$$\text{Per} = k_1 \sqrt{i}, \quad \text{(6)}$$

where $\text{Per}$ is the hydrogen permeability, $k_1$ is a constant, and $i$ is the corrosion current density. Hydrogen permeability is proportional to the iron ion activity because corrosion current density is proportional to the iron ion activity.

$$\text{Per} = k_2 \sqrt{a_{\text{Fe}^{2+}}}, \quad \text{(7)}$$

where $k_2$ is a constant. The hydrogen permeability was $2.5 \times 10^{-4}$ A/m for the H$_2$S partial pressure of 0.1 MPa at pH 5.3 in Fig. 5 and $1.0 \times 10^{-4}$ A/m for the H$_2$S partial pressure of 0.01 MPa at pH 6.0 in Fig. 6. The iron ion activity was calculated to be $1.6 \times 10^{-8}$ mol/L for the H$_2$S partial pressure of 0.01 MPa at pH 6.0 because the iron ion activity had already been calculated to be $1.0 \times 10^{-7}$ mol/L for the H$_2$S partial pressure of 0.1 MPa at pH 5.0. Therefore, the critical pH for the H$_2$S partial pressure of 0.01 MPa was also calculated to be 6.2. The calculated critical pH almost coincided with the measured critical pH value of 6.1 obtained from Fig. 6. Finally, the effect of H$_2$S partial pressure on the calculated and measured critical pH is summarized in Fig. 8. The calculated critical pH was expressed as Eq. (8).

$$\text{pH}_{\text{lim}} = -0.8 \log (P_{\text{H}_2\text{S}}) + 4.6, \quad \text{(8)}$$

where $P_{\text{H}_2\text{S}}$ represents the H$_2$S partial pressure (MPa).

**4.2. Prediction of Hydrogen Permeability for Various Sour Environments**

Previously, the effects of H$_2$S partial pressure and pH were investigated in the pH range from 3.0 to 5.0 using the same specimens of this study which corresponded to Steels A and B. Here, the relation between H$_2$S partial pressure and pH was summarized, by adding these previous studies of the relation between that H$_2$S partial pressure and pH in the pH range from 3.0 to 5.0. The effects of H$_2$S partial pressure and pH on hydrogen permeability after 96 h immersion which is considered to be steady state was indicated in Figs. 9 and 10. Hydrogen permeability decreased with decreasing H$_2$S partial pressure and increasing pH, as seen in Figs. 9 and 10. There were no difference in hydrogen permeation behavior for Steels A and B in the experimental condition of this study. Hydrogen permeability drastically decreased for H$_2$S partial pressure of 0.1 MPa and pH exceeding 5.5 and H$_2$S partial pressure of 0.01 MPa with pH exceeding 6.2 as seen in Fig. 10. That is, hydrogen permeability dramatically decreased over the critical pH, which makes iron sulfide stable. However, it is thought that hydrogen permeability does not decrease up to pH 7 for H$_2$S partial pressure of 0.001 MPa. From these results, hydrogen permeability was predicted and quantified for various sour environments using Eqs. (9) to (11).

$$\text{Per} = 7.1 + 0.96(1.4 \log (P_{\text{H}_2\text{S}}) - 0.51 \text{pH});$$

$$10^{-3} \text{MPa} \leq P_{\text{H}_2\text{S}} \leq 0.1 \text{MPa}; \quad 3 \leq \text{pH} \leq \text{pH}_{\text{lim}} \quad \text{(9)}$$

![Fig. 8. Relation between critical pH and H$_2$S partial pressure.](image)

![Fig. 9. Effect of H$_2$S partial pressure and pH on hydrogen permeability.](image)

![Fig. 10. Effect of H$_2$S partial pressure and pH on hydrogen permeability.](image)
5. Conclusions

Hydrogen entry behavior with different H$_2$S partial pressures exceeding pH 5.0 was investigated using API grade X65 line pipe and line pipe plate. Hydrogen entry into steel was predicted and quantified for various sour environments. The main conclusions were as follows.

(1) Hydrogen permeability dramatically decreased for H$_2$S partial pressure of 0.1 MPa exceeding pH 5.5. Hydrogen permeability also drastically decreased for H$_2$S partial pressure of 0.01 MPa exceeding pH 6.2. This phenomenon is caused by the formation of a stable film with iron sulfide. On the other hand, hydrogen permeability proportionally decreased with increasing pH for H$_2$S partial pressure of 0.001 MPa up to pH 6.0.

(2) The critical pH at which iron sulfide becomes quite stable was predicted from the equation of the relation among pH, H$_2$S partial pressure, and iron ion activity based on potential vs. pH in Fe–S–H$_2$O. Hydrogen concentration into steel invading from various sour environments was proposed and quantified.

REFERENCES