# Hydrogen Permeation of Pipeline Steel under Sour Condensate Film Condition

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### ABSTRACT

Hydrogen permeation behavior of pipeline steel under different sour condensate film condition was investigated by in-situ testing. The effects of H<sub>2</sub>S corrosion product scales and the temperature of wet gas containing a high content of hydrogen sulfide on the hydrogen permeation of pipeline steel were studied by electrochemical methods. In wet gas conditions with a high content of hydrogen sulfide, ambient pressure corrosion simulation experiments were conducted in Devanathan-Stachurski cell tests to analyze the effects of different corrosion product scales and temperatures on hydrogen permeation. The corrosion products were studied by X-ray diffraction (XRD) and scanning electron microscope (SEM). The results show that the current density related to hydrogen permeation decreased and corrosion product scales became more protective with time. Besides, the current density related to hydrogen permeation increased as the temperature of wet gas increased.

Key Word: hydrogen sulfide, sour condensate film, hydrogen permeation, pipeline steel

### INTRODUCTION

Pipeline steel has been widely utilized in the oil and gas transfer due to its high strength and ductility. However, the H<sub>2</sub>S present in the oil and gas has greatly worsened the metal pipe corrosion environment and at the same time, increased the risk of hydrogen induced cracking. Cracking accidents of pipelines caused by H<sub>2</sub>S have increased in recent years.<sup>1-5</sup> Although many international scholars have carried out a lot of work in this field, there is a lack of sufficient experience of corrosion of pipelines in wet gas containing high content of H<sub>2</sub>S. Therefore, corrosion and cracking related to pipeline environments that contain H<sub>2</sub>S and moisture has become more important in recent years. Corrosion or cracking of pipeline steel does not occur in H<sub>2</sub>S gas, it only occurs in wet H<sub>2</sub>S environments. Stress corrosion cracking of pipeline steel caused by hydrogen embrittlement can also occur in sour condensate film conditions.<sup>6</sup>

A wet  $H_2S$  environment may consist of either an aqueous solution or a condensed thin liquid film environment, where the latter is where corrosion cracking behavior of pipeline steel really occurs. The  $H_2S$  corrosion cracking behavior of pipeline steel under the two

environment is very different.<sup>7-9</sup>. Previous research based on simulated  $H_2S$  solutions for hydrogen permeation and corrosion has not revealed the corrosion cracking mechanism of pipeline steel under the condition of wet gas containing  $H_2S$ . For this research, in situ hydrogen penetration testing in wet  $H_2S$  conditions were conducted and the corrosion products have been analyzed to explore the hydrogen permeation rate and the corrosion products that occurred under the conditions of condensate sour film and changing temperature.

#### EXPERIMENT PROCEDURE

API<sup>(1)</sup> 5L X52QS pipeline steel was used in the experiments. The chemical composition of the steel is shown in Table 1. The steel specimens in the form of membranes were prepared having 0.6 mm thickness and 35 mm of diameter. The microstructure consists of ferrite and pearlite. Both sides of the membrane were ground with carborundum paper down to 1200 grit and polished. After pickling with 3 mol/L HCl, and degreasing with acetone, one side (detection side) of the steel membrane was deposited with a film of nickel in Watt's bath of 250 g/L NiSO<sub>4</sub>·7H<sub>2</sub>O + 45 g/L NiCl<sub>2</sub>·6H<sub>2</sub>O +40 g/L H<sub>3</sub>BO<sub>3</sub> using a cathodic current density of 10 mA/cm<sup>2</sup>.<sup>10</sup> In order to obtain different compositions of the corrosion product on the input side of the membrane, simulation corrosion experiments using the same experimental conditions as the hydrogen permeation tests (denoted by (1), (2), (3), and (4)) were conducted, as shown in Table 2, with specimens in the form of a diamond having 3 mm thickness and 1 mm of side length.

Hydrogen permeation experiments were performed by using an electrochemical permeation technique originally developed by Devanathan and Stachurski to determine the hydrogen permeation through steel membranes. The cell was composed of two compartments, a hydrogen generating cell (input side) and a hydrogen oxidizing cell (detection side). The detection side was held at a constant potential of 300 mV vs. SCE in 0.2 mol/L NaOH solution, under which conditions the steel was considered to be at a passive potential.

1. Once the passive current reached a constant value, the input side was heated and sour condensate film formed on the membrane surface. The input side was exposed in sour condensed film containing high content  $H_2S$  condition for a period lasting 14 d. At the same time, the current on the detection side was measured at set intervals, which gave a direct measurement of the hydrogen flow rate. Deoxygenation of the hydrogen oxidizing cell was carried out by purging with  $N_2$  for at least 8 hours.

2. Once the passive current reached a constant value, the input side was heated at different temperatures to get different sour condensate films formed on the membrane surfaces. The input side was exposed in sour condensed film containing high content  $H_2S$ 

<sup>&</sup>lt;sup>(1)</sup> American Petroleum Institute.

conditions for a constant period lasting about 5.5 h. At the same time, the current on the detection side was measured, which gave a direct measurement of the hydrogen flow rate. Deoxygenation of hydrogen oxidizing cell was carried out by purging with  $N_2$  for at least 8 hours.

Samples were characterized with a scanning electron microscope (SEM), an energy dispersive spectrometer (EDS) and an X-ray diffraction (XRD).

#### **RESULTS AND DISCUSSION**

#### Corrosion scales formed with exposure time

The XRD patterns of corrosion product film formed on the surface of API 5L X52QS steel at different corrosion time on the condition of wet gas are shown in Figure 2. All of the corrosion products are comprised of different types of iron sulfide, such as Mackinawite (FeS<sub>1-x</sub>) and Pyrrhotite (Fe<sub>1-x</sub>S). The diffraction peak of matrix is very high, indicating that the corrosion product is thin.

Figure 3 shows the SEM microphotography of the corrosion product film formed on the surface of API 5L X52QS steel at different exposure times. The surface morphology changed as the exposure time increased.

The initial corrosion scale was smooth and mainly consisted of amorphous Mackinawite (Fe<sub>1-x</sub>S, denoted by M), as shown in Figure 3(a), and it was already present after a 2 d exposure in wet gas containing  $H_2S$ .

Some areas of the specimens were not completely covered with a corrosion scale (image not shown). Those exposed for at least 8 d however, were completely covered. The temperature of the wet gas was low, leading to a low rate of anodic dissolution and corrosion products growth.

After 8 d exposure, the surface was complete covered with corrosion scale that had a very open and porous (sponge-like) structure, as shown in Figure 3(b). The corrosion scale was mainly consist of Mackinawite ((Fe<sub>1-x</sub>S, denoted by M).

After 12 d exposure, the surface was still completely covered with corrosion scale that had a very open and porous (sponge-like) structure with larger crystal size, as shown in Figure 3(c). Besides, the areas covered on the sponge-like corrosion scale became larger, the scale mainly consisted of Mackinawite and a little Pyrrhotite ( $Fe_{1-x}S+FeS_{1-x}$ , denoted by M+P).

Specimens exposed for 14 d had corrosion scale consisting of Mackinawite and little Pyrrhotite ( $Fe_{1-x}S + FeS_{1-x}$ , denoted by M+P) with layers, as shown in Figure 3(d).

## Effects of corrosion scales on hydrogen permeation behavior

The specimen was exposed to a sour condensate film for various periods of time up to 14 d, to get different corrosion scales on the specimen. Specimens with and without different corrosion scales were tested in the hydrogen permeation cells to measure the hydrogen permeation current density-time curves under free corrosion potentials with no cathodic charging on the input side, as shown in Figure 4. The thickness of the bare steel was 520  $\mu$ m. The background current density of bare steel was less than 1.0  $\mu$ A/cm<sup>2</sup>. The input side of the cell, containing deionized water, was heated at a temperature of 35 °C, then the high purity H<sub>2</sub>S gas was piped into the cell. The hydrogen permeation current appeared in a very short period time. For bare steel, amorphous Mackinawite scale, M scale, and M+P scale, the hydrogen permeation currents were 38.5  $\mu$ A/cm<sup>2</sup>, 29.8  $\mu$ A/cm<sup>2</sup>, 29  $\mu$ A/cm<sup>2</sup>, and 26.6  $\mu$ A/cm<sup>2</sup>, respectively. This indicates that the corrosion scales decreased the hydrogen concentration adsorbed on the surface. This means that under the condition of wet gas containing H<sub>2</sub>S, the corrosion product became more and more protective as the corrosion time increased at the temperature of 35 °C.

Related research<sup>11</sup> shows that for the same kind of material, the greater the hydrogen steady-state hydrogen permeation current is, the more severe the hydrogen damage is. According to the above test results, using the same conditions for hydrogen evolution, amorphous Mackinawite scale, M scale, and M+P scale, inhibited hydrogen adsorption on the surface in order. This indicates that these corrosion scales decrease the risk of hydrogen induced cracking for pipelines.

### Effects of temperature of wet gas on hydrogen permeation behavior

The hydrogen permeation current density-time curves of API 5L X52QS steel at different temperatures of wet gas containing H<sub>2</sub>S are shown in Figure 5. Table 3 shows the parameters of hydrogen permeation for API 5L X52QS steel at different temperatures of wet gas containing H<sub>2</sub>S, where  $i_{\infty}$  is steady-state hydrogen permeation current density,  $t_{0.63}$  is the time when  $i_t / i_{\infty} = 0.63$ ,  $J_{\infty}$  is steady-state hydrogen diffusion flux,  $\Phi$  is hydrogen permeability, and  $C^0$  is hydrogen concentration adsorbed on the surface. The thickness of the bare steel was 600 µm when the background current density of bare steel was less than 1.0 µA/cm<sup>2</sup>. The input side of the cell containing deionized water was heated to different temperatures, then the high purity H<sub>2</sub>S gas was piped into the cell. The hydrogen permeation current appeared in a very short period time indicating that hydrogen traps were filled up quickly.

The temperature of the wet gas became the main factor affecting hydrogen permeation. Increasing the temperature difference between the wet gas and the sample increased the condensation rate making ion in the corrosion reaction easier, which speeded up the

cathodic hydrogen evolution reaction. the rime for steady-state hydrogen permeation current is 839, 2173 and 1296 seconds respectively for increasing temperatures, indicating that the wet gas temperature delayed and then improved the absorption of hydrogen on the surface and the internal diffusion process, which increased and then decreased the balance time of the hydrogen diffusion. This produced steady-state hydrogen permeation current densities of 28.70  $\mu$ A/cm<sup>2</sup>, 67.20  $\mu$ A/cm<sup>2</sup> and 99.16  $\mu$ A/cm<sup>2</sup> in turn. The concentration of hydrogen adsorbed on the surface was 1.73  $\mu$ mol/cm<sup>3</sup>, 2.21  $\mu$ mol/cm<sup>3</sup>, and 3.16  $\mu$ mol/cm<sup>3</sup>, respectively, indicating that temperature promoted dissolution of gaseous H<sub>2</sub>S in the condensed liquid film and speeded up the cathodic hydrogen evolution reaction.

# CONCLUSIONS

In this paper, sour condensate film conditions were simulated, and the effects of different corrosion scales and temperature of wet gas on hydrogen permeation of pipeline steel at different periods were investigated. Several conclusions of this work are listed below:

- Under the condition of 35 °C wet sour gas, the formed corrosion scales changed from Mackinawite to Mackinawite and a little Pyrrhotite as corrosion time increased.
- Under the condition of 35 °C wet sour gas, the formed Mackinawite scale and Mackinawite and a little Pyrrhotite scale increasingly inhibited adsorption behavior of hydrogen in corrosion scale decreased the hydrogen concentration adsorbed on the surface in order.
- Increasing the temperature of the wet gas containing H<sub>2</sub>S could increase the steady-state hydrogen permeation current density which increases the risk of HIC of pipeline ranging from 20 °C to 50 °C.

### ACKNOWLEDGEMENTS

The project was supported by National Natural Science Foundation of China (Grant No. 51171022).

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C	Si	Mn	S	Р	Nb	Ti	Мо	V	Mn	Fe
0.11	0.27	1.1	0.0032	0.006	0.031	0.037	0.003	≤0.01	0.094	Bal.

Table 1Chemical Composition of Pipeline Steel (wt. %)

	pH₂S (MPa)	T (°C)	Corrosion Time (d)	Corrosion scale type
(1)	0.1	35	2	Amorphous Mackinawite (M)
(2)	0.1	35	8	Mackinawite(M)
(3)	0.1	35	12	Mackinawite +Little Pyrrhotite (M+P)
(4)	0.1	35	14	Mackinawite +Little Pyrrhotite (M+P)

 Table 2

 Conditions for the Preparation of Corrosion Scales

Table 3Parameters of hydrogen permeation for API 5L X52QS steel at different<br/>temperatures of wet gas

T (°C)	i <sub>∞</sub> (µA/cm²)	$J_{\infty}$ (×10 <sup>-11</sup> mol H/cm <sup>2</sup> /s)	Φ (×10 <sup>-12</sup> mol H/s/cm)	<i>C<sup>0</sup></i> (10 <sup>-5</sup> mol/cm <sup>3</sup> )	<i>H<sub>m</sub></i> (10 <sup>-5</sup> mol)
20	28.70	29.74	1.78	1.73	6.52
35	67.20	69.63	4.18	2.21	8.33
50	99.16	102.76	6.17	3.16	11.9



Figure 1: Microstructure of API 5L X52QS pipeline steel

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Figure 2: XRD patterns of corrosion product films formed on the surface of API 5L X52QS steel at different corrosion times



Figure 3: Surface morphology of five kinds of corrosion scales: (a) 5 d; (b) 8 d; (c) 14 d;

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Figure 4: Hydrogen permeation curves of the sample with and without corrosion scales



Figure 5: Hydrogen permeation curves of the sample at different temperatures of wet gas