

The Effect of H₂S and Cl⁻ on Hydrogen Permeation in High Strength Low Alloy Carbon Steels

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ABSTRACT

The objective of this research is to obtain a quantitative description of the effect of adsorbed H₂S and chloride on the hydrogen penetration in high strength low alloy (HSLA) carbon steel, by evaluating the response of hydrogen permeation current and the formation of characteristic inductive response using hydrogen permeation and electrochemical Impedance spectroscopy methods on HSLA carbon steel C110.

The hydrogen permeation flux measured in Devanathan-Stachurski cell suggests that enhance effect of H₂S on absorption of hydrogen following an adsorption isotherm behavior as a function of the H₂S activity in solution. The inductive response of electrochemical impedance spectroscopy (EIS) showed consistency with effect of adsorption of H₂S. The EIS results also indicate that the coverage of H₂S was suppressed by chloride. A good correlation about the effect of adsorbed chloride was found between inductive response and hydrogen permeation flux.

Key words: hydrogen permeation, H₂S, chloride, pH value, adsorption, electrochemistry, carbon steel

INTRODUCTION

HSLA steels play an important role in oil and gas storage and transportation, where H₂S and water exist in¹⁻⁴. However, the application of HSLA steel is limited by corrosion and mechanical problems exposure to wet H₂S environment, e.g., HIC and sulfide stress cracking (SSC)⁵.

A recent study⁶ shows that, by adjusting the brine ionic strength, it is possible to obtain different values of the threshold stress intensity parameter K_{ISSC} at the same concentration of dissolved H₂S or H₂S fugacity. It was suggested that the explanation for that behavior is due to the relationship between the

K_{SSC} and the subsurface hydrogen concentration which is heavily dependent on the coverage of the metal surface by absorbed H_2S as indicated by Cancio et al^{7,8}. The relevant aspect is that at constant brine strength and pH the H_2S coverage on the steel surface is controlled by the H_2S activity. The interaction between the H_2S contained within the corrosive environment and the low alloy steel interface is the subject of many studies in the literature⁹⁻¹¹, the consensus indicates that a layer of adsorbed H_2S or containing sulfides is formed depending the H_2S concentration and the solution pH¹²⁻¹⁴. The role of the adsorbed layer of H_2S or sulfide appears to be critical to understand the hydrogen permeation behavior in HSLA steels which show that the apparent diffusion coefficient that reflects the effect of the sulfide layer, affects to the susceptibility for SSC cracking¹⁵. The results from literature propose that the role of H_2S in promoting hydrogen uptake in the steel occurs either by suppressing the hydrogen recombination reaction at metal surface, or by catalyzing hydrogen absorption through the presence of the sulfide layer.^{16,17} The relationship between this factors and the C_0 can be expressed in the following way:¹⁸

$$C_0 \propto J_{\text{corr}}(T, \text{H}_2\text{S}, \text{H}^+) f(\theta_s, T) \quad (1)$$

where: T is temperature, H_2S and H^+ stand for the hydrogen sulfide and proton concentration in the environment, θ_s is the adsorbed H_2S coverage thorough which the catalytic effect on hydrogen absorption occurs.

Although there are no clear, experimental results reported in relation to the details of the adsorption isotherm for H_2S on polycrystalline iron (or steel), the results reported in the literature clearly shows that hydrogen uptake in steel increases with the H_2S concentration and with decreasing solution pH at room temperature, which increases SSC susceptibility¹⁹⁻²¹.

The objective of this research is to quantitatively describe the impact of adsorbed H_2S and NaCl on hydrogen uptake in HSLA steel C110, by evaluating the response of hydrogen permeation and the formation of characteristic inductive response by electrochemical methods.

The presence of the inductive term in the equivalent circuit is associated of the presence of an adsorbed species as part of the electrode kinetics involved in either the cathodic or anodic current process at near open circuit conditions. Assuming only one species adsorbed on the surface, the surface coverage relationship with the inductive term is detailed in the literature as follows:

$$\theta = \frac{k_b k_f \beta + k_f^2 \beta}{(k_b - k_f)(k_b(1-\beta) + k_f \beta)} + \frac{\sigma RT}{(k_b - k_f)(k_b(1-\beta) + k_f \beta)L} \quad (2)$$

In Eq. (2), θ is surface coverage of adsorbed item, β is the symmetry constant for the adsorption reaction $\sigma = F\Gamma^\infty$ which is the charge for $\theta=1$, R is the universal gas constant, T is the temperature (K) and L is the inductive term of the equivalent circuit. k_f and k_b are the adsorption and desorption rate constants. Therefore, if hydrogen uptake is accelerated by the catalytic effect of adsorbed H_2S on adsorption of hydrogen, then, a characteristic correlation between hydrogen uptake and atomic hydrogen coverage on the surface, which can be characterized by C_0 and L , can be found that depends on adsorption of H_2S .

EXPERIMENTAL PROCEDURE

Experimental design

Following the objectives of the present study an experimental design was developed to evaluate the individual effects of the H_2S activity and the NaCl concentration in aqueous solution on the hydrogen penetration behavior in HSLA steels. The experiment sequence contemplated for the present study is summarized in Table 1, as it can be appreciated the evaluation is centered on the separate effects of the H_2S content in solution and the NaCl concentration in the brine.

The independent variables in the experiments contemplated in the study of the H_2S effect on the hydrogen penetration, are the H_2S concentration in the gas phase and the solution pH, keeping constant the brine Cl^- concentration. In the case of the evaluation of the NaCl content effect, the independent variable is the NaCl concentration whereas the pH and the H_2S content are kept constant. The depend

variable in our study are the hydrogen permeation rate and the EIS spectra obtained from corroding surface of the OCTG grade HSLA steel C110.

Table 1: The Sequence of Experimental Conditions

	H ₂ S (mole% gas)	NaCl (M)	pH
Effect of H ₂ S	0.01 - 90	1	3.5 & 5.5
Effect of NaCl	1	1 - 20	3.5

Materials

The material used in this study is HSLA steel C110, the composition is shown in Table 2. Before testing, C110 was baked at 200 °C for 8 hours to remove the trapped hydrogen in it. The surface of specimen was polished to 600 grits to eliminate the effect of surface roughness on hydrogen permeation.

Table 2: Chemical Composition of C110 in wt%

Element	C	Mn	Mo	Cr	Ni	P	S
Min.	-	-	0.250	0.400	-	-	-
Max.	0.350	1.200	1.000	1.500	0.990	0.020	0.005

Hydrogen Permeation

Hydrogen permeation testing was conducted at 1 atm and 25 °C using Devanathan-Stachurski system according to ASTM G148-97 (2018)⁽¹⁾. As shown in Figure 1, Devanathan-Stachurski system is composed by twin cells separated by C110 membrane with thickness of 0.02 ± 0.005 cm and exposed area of 7.06 cm^2 .

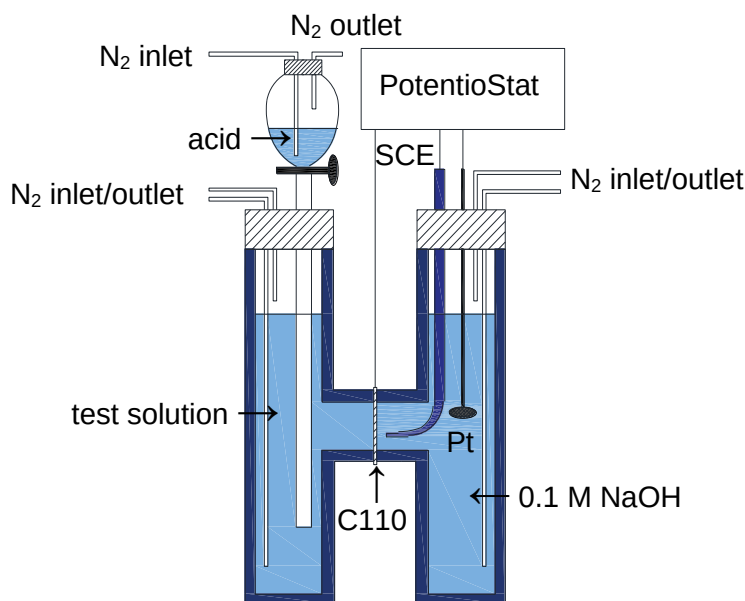


Figure 1: Devanathan_Stachurski Cell

The procedure can be described as following. Before assembly, the right side of the polished membrane was electroplated by nickel in Watt bath ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$: 45 g/L, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$: 240 g/L, H_3BO_3 : 40 g/L). A cathodic current of 0.0043 A/cm^2 was applied on the membrane during nickel plating. During measurement, the right cell was bubbled by N_2 and a voltage of + 300 mV (vs. SCE) was applied. The Na_2S solution in left cell and acid (hydrochloride acid and acetic acid with specific proportion) in funnel

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was deaerated by N₂ for 1 hour before mixing to generate H₂S. The current output of right cell was recorded as hydrogen permeation current.

H₂S activity was calculated from H₂S concentration using OLI Studio. The hydrogen permeation flux J(t) was calculated from hydrogen permeation current I by Eq. (3):

$$J(t) = I/(AF) \quad (3)$$

where I refers to hydrogen permeation current (A), A is immersion area (cm²) and F is Faraday constant. And sub-surface atomic hydrogen concentration C₀ can be described by Eq. (4):

$$C_0 = (J_{ss} \cdot L_{C110})/D_{eff} \quad (4)$$

$$D_{eff} = L_{C110}^2/(6 \cdot t_{lag}) \quad (5)$$

where J_{ss} is atomic hydrogen permeation flux at steady-state (mol/s/cm²), L_{C110} is thickness of membrane (cm), D_{eff} is effective diffusivity of atomic hydrogen (cm²/s), which is defined by Eq. (5), where t_{lag} is the time to achieve a value of J(t)/J_{ss} = 0.63 (s).²¹

EIS Measurement

EIS measurement was carried out in electrochemical cell at 1 atm and 25 °C. The environment in the cell was same with the environment of left cell for hydrogen permeation. Three-electrode system was utilized in EIS measurement comprising working electrode C110 cylinder (length: 4.37 ± 0.05 cm, diameter: 0.64 ± 0.05 cm and immersion area: 6.07 cm²), W/WO₃ reference electrode and Pt counter electrode. Na₂S solution and acid was first purged of O₂ by N₂ for 40 minutes separately before mixing to create H₂S. EIS measurement was carried out 30 minutes after H₂S created. A perturbation with voltage of 10 mV (vs. OCP) and frequency of 10000 Hz to 0.01 Hz was applied to the testing system.

RESULTS

Effect of H₂S Activity and pH Value

The atomic hydrogen permeation flux J(t) curves in 1 wt% NaCl solution at pH 3.5 and 5.5 with varying H₂S concentration are shown in Figure 2. A decrease in H₂S concentration and pH value resulted in a decrease in hydrogen permeation flux. This indicates H₂S can enhance the hydrogen uptake of C110. And this effect was more noticeable in pH 3.5 than in pH 5.5. This could be caused by the compact iron sulfide film formed on the surface at pH 5.5 which blocked hydrogen absorption partly.²²

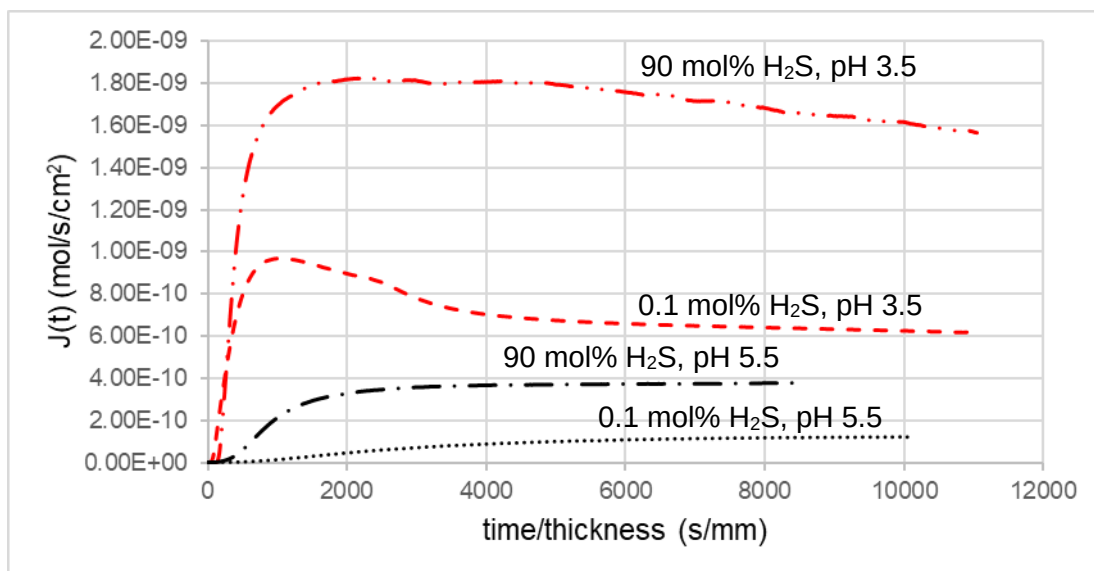


Figure 2: Effect of H₂S Activity and pH Value on Hydrogen Permeation for C110 in 1 wt% NaCl