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Contribution of CO₂ on hydrogen evolution and hydrogen permeation in low alloy steels exposed to H₂S environment

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Summary

Hydrogen charging in low alloy steels is a major problem in oil and gas environments containing hydrogen sulfide (H₂S). The risk of sulfide stress cracking (SSC) is usually determined from the values of water pH and H₂S partial pressure (P_{H_2S}). The goal of the present study is to check if hydrogen charging is influenced by other parameters than the sole pH and P_{H_2S} , and especially by carbon dioxide (CO₂). Experiments engaged the measurement of hydrogen permeation through thin mild steel membranes under potentiometric control. Charging solutions with different H₂S concentrations with or without CO₂ were used, in order to examine their individual contributions to the charging flux.

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1 Introduction

The risk of hydrogen embrittlement of steels is a primary concern for material selection in oil and gas production. The presence of H₂S enhances hydrogen charging in the steel and thus increases the risk of hydrogen embrittlement. Sulfide stress cracking (SSC) is one of the main risks of steel failures in H₂S environments. Hydrogen flux through the steel surface is the driving force for this mode of cracking [1,2]. P_{H_2S} and pH are considered to be the main parameters controlling SSC [3]. Thus, materials testing for use in oil and gas environments containing H₂S is often performed in solutions with P_{H_2S} and pH simulating field conditions. Although several indirect experimental facts indicate that the ratio between CO₂ and H₂S could influence SSC severity, it is hardly taken into account in most laboratory studies or in materials qualification procedures. Depending on local practices, hydrogen permeation studies are performed with H₂S gas mixed with N₂ [4,5] or with CO₂ [6]. The same holds for SSC cracking tests by oil and gas operators or steel suppliers. However, CO₂ is known to have a strong impact on corrosion. It is well known that the cathodic reaction rate is enhanced in aqueous solutions containing dissolved CO₂, in comparison with strong acid solutions at the same pH [7-11]. In addition to its impact on global electrochemical kinetics, CO₂ might also have a direct contribution to the hydrogen charging mechanism. Competitive adsorption between sulfur compounds and other anions such as bicarbonates or carbonates could modify the net charging flux [1].

The intent of this paper was to check if CO₂ has an impact on hydrogen charging in steel exposed to water containing dissolved H₂S. Hydrogen permeation measurements were performed on thin steel membranes exposed to test solutions at controlled pH, and with different ratios of CO₂ and H₂S.

2 Material and methods

2.1 Tested Material

Permeation membranes were machined from a C125 sour service pipe. Membrane thickness was 0.5 mm, and the exposed surface was 17.3 cm².

Before each experiment, both faces of the membrane were grinded to SiC paper grit 2500 then degreased in acetone and dried ethanol. The exit face was then coated with palladium to ensure an optimized electrochemical hydrogen extraction [12]. The estimated thickness of the palladium layer is 0.1 μm.

2.2 Corrosive medium

The corrosive environment was chosen to shed light on the impact of CO₂ / H₂S ratio on hydrogen charging. The support electrolyte contained 0.1 mol.L⁻¹ potassium perchlorate (KClO₄). pH of the test solution was continuously maintained at a

constant value of 4.5 with addition of 1 mol.L⁻¹ potassium hydroxide (KOH) or 0.05N perchloric acid (HClO₄). Dissolved H₂S and CO₂ content were kept constant by continuous purging gas mixtures containing 0 to 5 mol.% H₂S balanced with either N₂ or CO₂. All tests were performed at atmospheric pressure.

Dissolved oxygen was strictly removed by efficient de-aeration of test solutions and N₂ purging of the test cells before each experiment.

2.3 Permeation set up

Electrochemical permeation measurements were performed with a Devanathan-Stachurski cell [13] at ambient temperature.

In order to control precisely the electrochemical reactions at the entry face, cathodic potential sweeps were applied at the charging face. Measurements were performed under potentiostatic control, until stabilization of both the cathodic current (J_{cath}) in the charging cell and the permeation current (J_{perm}) in the extraction cell. Potential sweep was started at the more cathodic potential and up to the open current potential. In order to avoid the pollution of the charging solution by the products of the anodic reaction, the counter-electrode was placed in another compartment separated by a salt-bridge.

The exit surface of the membrane was held in a de-aerated 0.1 mol.L⁻¹ NaOH solution and polarized to an anodic potential of 350mV vs. Hg/HgO reference electrode with 1 M KOH electrolyte, providing a direct measurement of the hydrogen flux crossing the steel membrane.

This procedure allows a direct measurement of the permeation efficiency ($Perm_{eff}$), defined as the ratio between J_{perm} and J_{cath} . Cathodic polarization also avoids the precipitation of iron sulfide or iron carbonate on the steel entry side which proceed rapidly at the corrosion potential (E_{corr}) in CO₂ and H₂S environments.

3 Results and discussion

For all experiments, E_{corr} is close to -650 to -700 mV vs Ag/AgCl. The impact of CO₂ and H₂S on the cathodic current is illustrated in Figure 1.

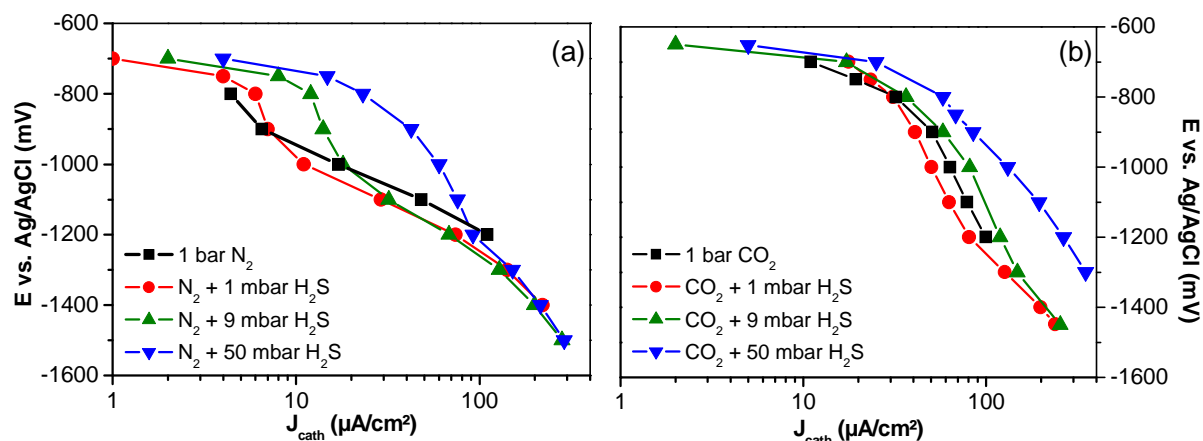


Figure 1 : Polarization curves of the entry face of steel membrane in de-aerated aqueous solutions for various H_2S concentrations without CO_2 (a) and with CO_2 (b).

When H_2S is the only acid gas present in the system, J_{cath} exhibits a strong increase with P_{H_2S} (Figure 1 a). The shape of the current – potential curves suggests a mass transport limitation in the potential domain close to E_{corr} . Previous studies in comparable environments have shown that this current plateau could be attributed to the diffusion limited proton reduction, and also to the transport of H_2S with subsequent H_2S reduction [14-16].

For the more cathodic potentials, water reduction becomes the dominant contributor to J_{cath} .

When CO_2 is added, J_{cath} increases sharply (Figure 1 b). This phenomenon has already been discussed widely in the literature with different theories [7-9,17-19]. In a recent work, Remita et al. have shown that the additional cathodic current associated with CO_2 could entirely be explained by the transport of carbonic acid followed by its dissociation close to the surface [19]. This mechanism corresponds to a buffering effect, where the weak acid acts as a reservoir of additional protons available at the steel surface by the chemical dissociation reactions. With 1 bar CO_2 and for the different levels of P_{H_2S} used for this study, the influence of P_{H_2S} on J_{cath} is low, in particular in the potential region close to E_{corr} .

The impact of CO_2 and H_2S on the permeation current density is illustrated in Figure 2.

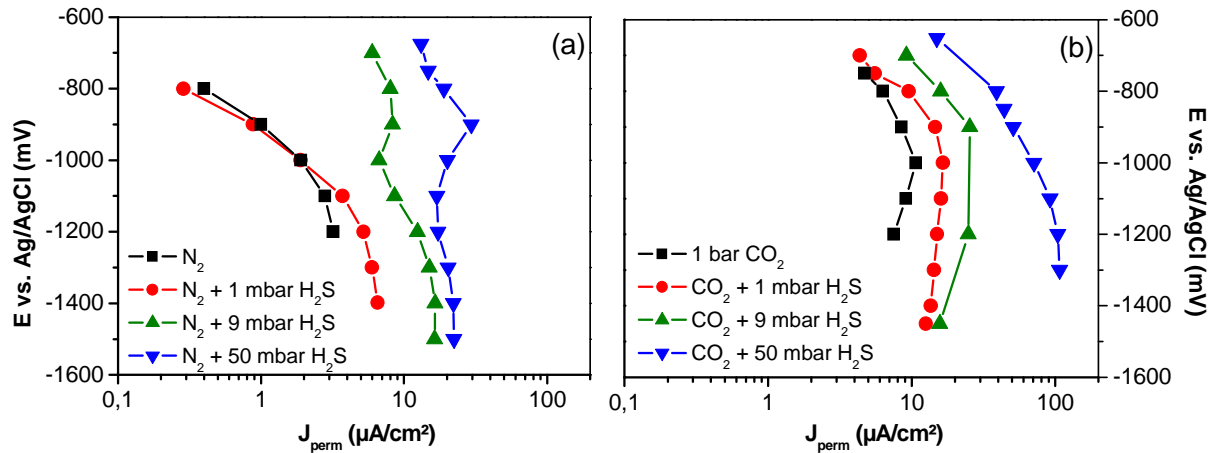


Figure 2 : Evolution of the hydrogen permeation current density with the potential of the entry face exposed to de-aerated aqueous solutions for various H₂S concentrations without CO₂ (a) and with CO₂ (b).

It appears that both CO₂ and H₂S have a strong impact on hydrogen permeation in the steel. J_{perm} always increases with $P_{\text{H}_2\text{S}}$, independently of the presence of CO₂. It is also interesting to note that the impact of 1 mbar H₂S is extremely moderate in comparison with test solutions containing no H₂S. This result is in excellent agreement with industrial practices for testing the susceptibility of steels to sulfide stress cracking (SSC), which consider that the risks of SSC vanish below 3 mbar of H₂S [3].

We also observe in Figure 2 that for a given $P_{\text{H}_2\text{S}}$, the presence of CO₂ always results in higher permeation current density. This trend is similar to the cathodic current density at the entry face (Figure 1). However, close to E_{corr} , the amplitude of the increase of J_{perm} is particularly important at the low $P_{\text{H}_2\text{S}}$. It is quite remarkable that this effect is also observed in the absence of H₂S, suggesting that CO₂ also promotes hydrogen entry in the steel, though with a much lower efficiency than H₂S. A similar effect of bicarbonate ions had already been inferred by Dean and by Asher and Singh [20,21].

In order to illustrate the impact of the polarization of the entry face, $Perm_{eff}$ was calculated for each potential value. The results are plotted in Figure 3.

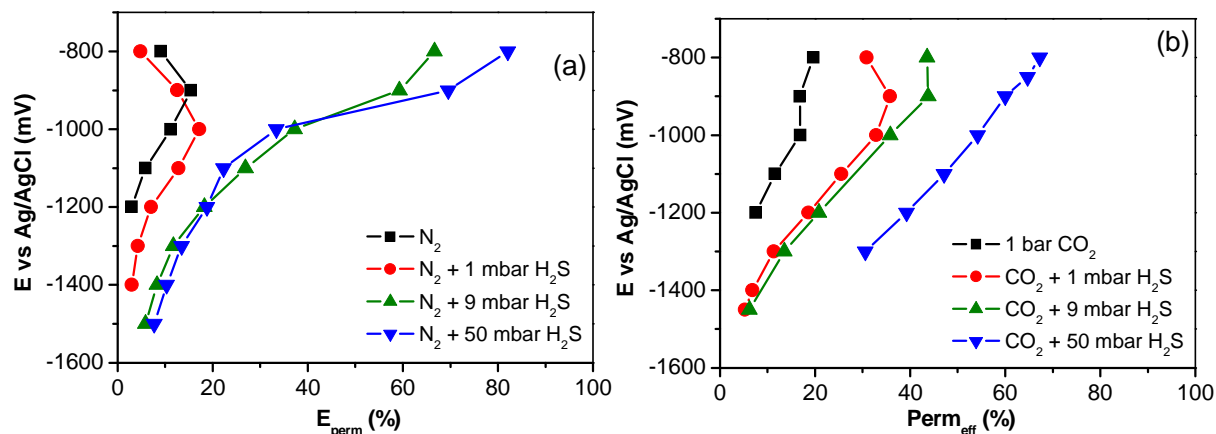


Figure 3 : Evolution of the permeation efficiency with the potential of the entry face exposed to de-aerated aqueous solutions for various H_2S concentrations without CO_2 (a) and with CO_2 (b).

It appears that $Perm_{eff}$ rapidly decreases when the cathodic potential is decreased. However, this decrease is less marked with CO_2 . Similar results were obtained several decades ago by Le Boucher [22] who explained that the decrease of permeation efficiency corresponded to a change in the cathodic reaction at the entry face, from the proton or the H_2S reduction (1 or 2) to water reduction.

On the other hand, when the potential of the entry face is close to the corrosion potential, the permeation efficiency can reach very high values. In test solutions with 9 or 50 mbar H_2S , permeation efficiency at the corrosion potential could reach 50 to 100%. This indicates that nearly all protons reduced at the entry face during the corrosion process permeate and diffuse through the steel. For these H_2S concentrations, the impact of CO_2 on the permeation efficiency is moderate. However, for the low P_{H_2S} values, the permeation efficiency in the potential region close to E_{corr} is clearly influenced by CO_2 . While hydrogen permeation is negligible in the absence of CO_2 , a significant part of the proton reduced at the entry face is absorbed and permeates through the membrane when CO_2 is present. This result suggests that CO_2 has a direct impact on the charging mechanism, at least when P_{H_2S} is moderate or null. Electrochemical impedance spectroscopy or modulated permeation could be used to study the charging process in more details [23–26].

4 Conclusion

Sulfide stress cracking is a major issue for low alloy steel components used in oil and gas environments containing H_2S . To date, the evaluation of steel resistance to SSC considers only the pH and P_{H_2S} of the environment. Although CO_2 is always present in sour fields, its impact on SSC cracking is still poorly understood. This work investigated the impact of CO_2 on hydrogen evolution and hydrogen charging in steel exposed to acid water at pH 4.5 and with various P_{H_2S} .

Near E_{corr} , Hydrogen evolution reaction was found to increase considerably with CO_2 and H_2S , in comparison with a test solution of dilute strong acid at the same pH. A similar increase of hydrogen permeation into the steel membrane was observed when CO_2 and H_2S partial pressure were increased. The influence of CO_2 was strongly lowered at high H_2S concentration.

At large negative overpotentials, most of hydrogen is evolved and the permeation efficiency decreases drastically.

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