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Cécile Plennevaux, Jean Kittel, Marion Frégonèse, Bernard Normand, Francois Ropital, et al.. Contribution of CO<sub>2</sub> on hydrogen evolution and hydrogen permeation in low alloy steels exposed to H<sub>2</sub>S environment.. Electrochemistry Communications, Elsevier, 2012, 8 p. <10.1016/j.elecom.2012.10.010>. <hal-00743294>

**HAL Id: hal-00743294**

**<https://hal-ifp.archives-ouvertes.fr/hal-00743294>**

Submitted on 26 Oct 2012

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## Contribution of CO<sub>2</sub> on hydrogen evolution and hydrogen permeation in low alloy steels exposed to H<sub>2</sub>S environment

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### Summary

Hydrogen charging in low alloy steels is a major problem in oil and gas environments containing hydrogen sulfide (H<sub>2</sub>S). The risk of sulfide stress cracking (SSC) is usually determined from the values of water pH and H<sub>2</sub>S 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 (CO<sub>2</sub>). Experiments engaged the measurement of hydrogen permeation through thin mild steel membranes under potentiometric control. Charging solutions with different H<sub>2</sub>S concentrations with or without CO<sub>2</sub> 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 H<sub>2</sub>S 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 H<sub>2</sub>S 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 H<sub>2</sub>S is often performed in solutions with  $P_{H_2S}$  and pH simulating field conditions. Although several indirect experimental facts indicate that the ratio between CO<sub>2</sub> and H<sub>2</sub>S 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 H<sub>2</sub>S gas mixed with N<sub>2</sub> [4,5] or with CO<sub>2</sub> [6]. The same holds for SSC cracking tests by oil and gas operators or steel suppliers. However, CO<sub>2</sub> 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 CO<sub>2</sub>, in comparison with strong acid solutions at the same pH [7-11]. In addition to its impact on global electrochemical kinetics, CO<sub>2</sub> 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 CO<sub>2</sub> has an impact on hydrogen charging in steel exposed to water containing dissolved H<sub>2</sub>S. Hydrogen permeation measurements were performed on thin steel membranes exposed to test solutions at controlled pH, and with different ratios of CO<sub>2</sub> and H<sub>2</sub>S.

## 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 cm<sup>2</sup>.

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 CO<sub>2</sub> / H<sub>2</sub>S ratio on hydrogen charging. The support electrolyte contained 0.1 mol.L<sup>-1</sup> potassium perchlorate (KClO<sub>4</sub>). pH of the test solution was continuously maintained at a

constant value of 4.5 with addition of 1 mol.L<sup>-1</sup> potassium hydroxide (KOH) or 0.05N perchloric acid (HClO<sub>4</sub>). Dissolved H<sub>2</sub>S and CO<sub>2</sub> content were kept constant by continuous purging gas mixtures containing 0 to 5 mol.% H<sub>2</sub>S balanced with either N<sub>2</sub> or CO<sub>2</sub>. All tests were performed at atmospheric pressure.

Dissolved oxygen was strictly removed by efficient de-aeration of test solutions and N<sub>2</sub> 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.

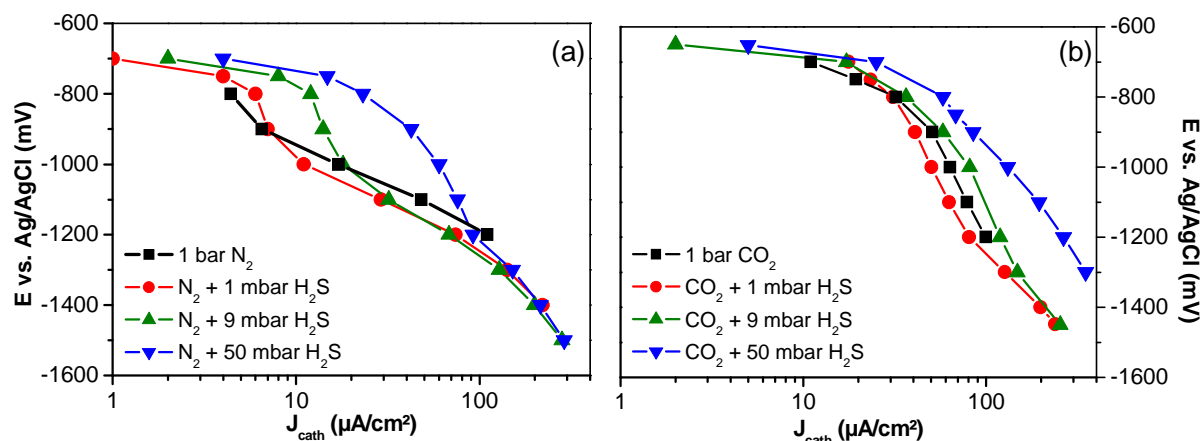
In order to control precisely the electrochemical reactions at the entry face, cathodic potential sweeps were applied at the charging face. Measurements were performed under potentiostatic control, until stabilization of both the cathodic current ( $J_{cath}$ ) in the charging cell and the permeation 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<sup>-1</sup> 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 CO<sub>2</sub> and H<sub>2</sub>S environments.

## 3 Results and discussion

For all experiments,  $E_{corr}$  is close to -650 to -700 mV vs Ag/AgCl. The impact of CO<sub>2</sub> and H<sub>2</sub>S on the cathodic current is illustrated in Figure 1.



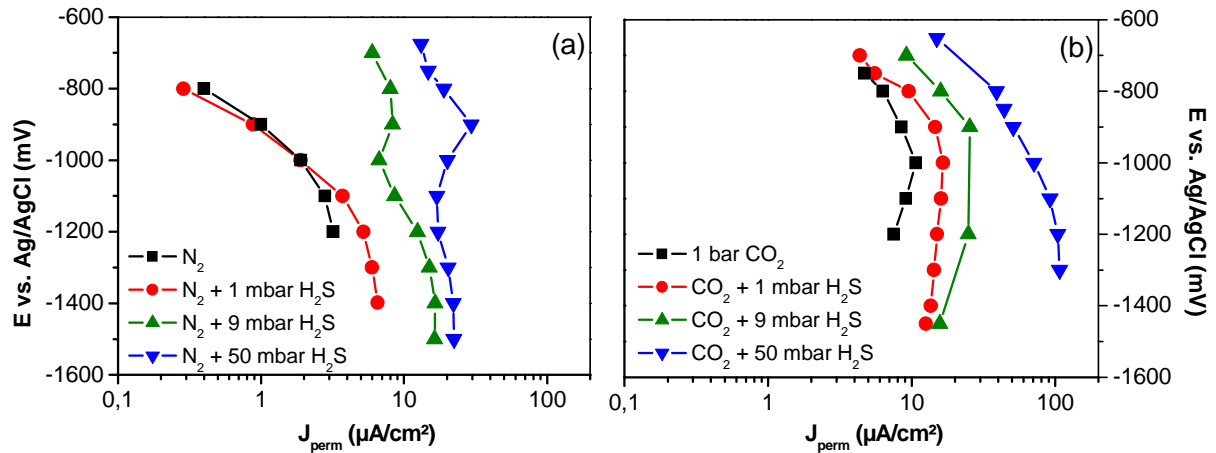
**Figure 1 : Polarization curves of the entry face of steel membrane in de-aerated aqueous solutions for various  $H_2S$  concentrations without  $CO_2$  (a) and with  $CO_2$  (b).**

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.

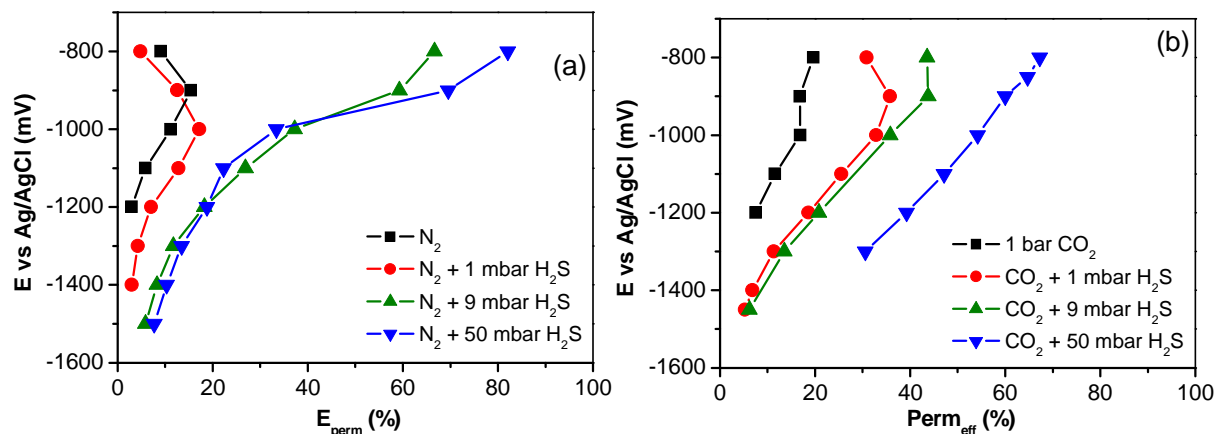


**Figure 2 : Evolution of the hydrogen permeation current density with the potential of the entry face exposed to de-aerated aqueous solutions for various  $\text{H}_2\text{S}$  concentrations without  $\text{CO}_2$  (a) and with  $\text{CO}_2$  (b).**

It appears that both  $\text{CO}_2$  and  $\text{H}_2\text{S}$  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  $\text{CO}_2$ . It is also interesting to note that the impact of 1 mbar  $\text{H}_2\text{S}$  is extremely moderate in comparison with test solutions containing no  $\text{H}_2\text{S}$ . 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  $\text{H}_2\text{S}$  [3].

We also observe in Figure 2 that for a given  $P_{\text{H}_2\text{S}}$ , the presence of  $\text{CO}_2$  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  $\text{H}_2\text{S}$ , suggesting that  $\text{CO}_2$  also promotes hydrogen entry in the steel, though with a much lower efficiency than  $\text{H}_2\text{S}$ . 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  $\text{CO}_2$  and  $\text{H}_2\text{S}$ , 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  $\text{CO}_2$  and  $\text{H}_2\text{S}$  partial pressure were increased. The influence of  $\text{CO}_2$  was strongly lowered at high  $\text{H}_2\text{S}$  concentration.

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

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