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F. Grosjean, J. Kittel

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Hydrogen charging in low alloy steels exposed to H₂S: impact of CO₂ or N₂ in the gas mixture.

C. Plennevaux, T. Cassagne
TOTAL, Avenue Larribau, Pau Cedex 64018, FRANCE

M. Frégonèse, B. Normand
MATEIS, INSA de Lyon, CNRS UMR 5510, Avenue Jean Capelle, Villeurbanne Cedex
69621, FRANCE

J. Kittel, F. Ropital, F. Grosjean
IFP Énergies nouvelles, Rond-point de l'échangeur de Solaize BP3, 69360 Solaize, France

Summary

This paper examines the influence of CO₂ / H₂S ratio on hydrogen charging in low alloy steels. Hydrogen flux through the steel surface is the driving force for sulfide stress cracking (SSC). The impact of H₂S and pH on SSC severity is extremely well documented, and these two parameters are used in the SSC severity diagram of ISO 15156-2 [1]. However, the CO₂ / H₂S ratio is not considered in standard SSC testing procedures, even though it has a strong impact on corrosion. Indeed, according to several authors, competitive adsorption between HS⁻ and HCO₃⁻ on the steel surface could modify the charging flux, thus the SSC risks.

The goal of the present study was to check if hydrogen charging is influenced by other parameters than the sole pH and P_{H₂S}. Experiments consisted in hydrogen permeation measurements through HSLA steel thin membranes. They were performed under cathodic charging in order to avoid corrosion products precipitation. Charging solutions with different H₂S concentrations with or without CO₂ were used, in order to examine the individual contributions to the charging flux, and hence to evaluate a possible impact on SSC risks.

1 Introduction

The risk of hydrogen embrittlement of steels is one of the main concerns for materials selection in oil and gas industry. In particular, the presence of hydrogen sulfide enhances hydrogen charging in the steel and thus increases the risk of hydrogen embrittlement. Different mechanisms of hydrogen cracking may occur in sour conditions and in particular:

- Hydrogen Induced Cracking (HIC), characterized by internal cracks caused by hydrogen recombination at microstructural traps in the steel. Cracks can be generated even after immersion in the hydrogenated medium.
- Sulfide Stress Cracking (SSC), initiated at the steel surface. An applied stress is required when the steel is immersed in the H₂S containing medium. The driving force is the hydrogen flux at the steel surface.

Hydrogen permeation is a proper technique for the study of hydrogen interactions with steel. In the present paper, it is used mainly to examine the interactions between the aqueous environment and the hydrogen charging process, which governs SSC cracking.

Sulfide stress cracking is strongly influenced by environmental conditions at the steel surface. Impacts of P_{H₂S} and pH are the main parameters controlling SSC. This is illustrated in the pH vs. P_{H₂S} severity diagram of ISO 15156-2 [1]. This diagram is commonly used for the selection of carbon steels for H₂S service. Materials testing is often performed by laboratory tests in solutions with P_{H₂S} and in-situ pH simulating field conditions. Carbon dioxide is only taken into account indirectly through the pH calculation.

Nevertheless CO₂ is already known to have a stronger impact on corrosion compared with other acid solutions at the same pH. This is because it enhances the Hydrogen Evolution Reaction (HER). Recent investigations [2] showed that this observation can be attributed to the buffering effect of CO₂. In other words, due to its ability to dissociate according to equations (a) and (b), the dissolved CO₂ acts as a reservoir of additional protons available for the HER. As a consequence, carbon dioxide might influence the hydrogen charging in the steel.



The presence of CO₂ can also influence surface reactions [3]. Indeed bicarbonates produced by reaction (a) may eventually adsorb on the metal surface. Thus

depending on the $\text{CO}_2 / \text{H}_2\text{S}$ ratio, a competition between HCO_3^- and HS^- adsorptions might occur influencing the hydrogen charging process.

Most of the time, application specific tests are performed at ambient pressure with gas mixtures containing H_2S at the expected $P_{\text{H}_2\text{S}}$, completed by CO_2 . Additionally N_2 is sometimes used instead of CO_2 by some laboratories but the difference between both practices is not really established.

The ISO 15156 SSC diagram could also be drawn with $P_{\text{H}_2\text{S}} / P_{\text{CO}_2}$ ratio on the X-axis instead of $P_{\text{H}_2\text{S}}$. For experiments under 1 bar total pressure, the range of $P_{\text{H}_2\text{S}} / P_{\text{CO}_2}$ varies from nearly zero (low $P_{\text{H}_2\text{S}}$ and P_{CO_2} close to 1 bar) to infinity (1 bar H_2S without CO_2 , on the far right of the diagram).

In addition to the interpretation of the SSC diagram, the intent of this paper provides experimental data in order to discuss if the use of CO_2 or N_2 as balanced gas gives equivalent SSC risks. The next and even more important question is the representativity of the laboratory conditions: ideally, laboratory solutions should reproduce or at least over-estimate the severity of field conditions.

In this paper, the impact of $\text{CO}_2 / \text{H}_2\text{S}$ ratio on hydrogen charging is studied. Permeation measurements are performed on thin membranes in order to assess the consequences on the SSC severity diagram.

2 Experimental procedure

2.1 Tested Material

All permeation membranes were machined from a C125 sour service pipe. The membrane thickness was 0.5 mm, and the exposed surface was 17.3 cm². Before each experiment, both faces of the membrane were manually polished to grade 2500 and cleaned in acetone and ethanol using an ultrasonic cleaning bath. The exit face was then coated with palladium to ensure a correct extraction of hydrogen by the electrochemical detection device [4-6].

According to previous studies in sour environment [7-9], this membrane thickness ensures a control of the hydrogen permeation by the charging process. Permeation current density is then independent of membrane thickness, and according to Crolet [7], its value corresponds to the net charging flux. It is then well fit for the study of hydrogen charging, since it minimizes the contribution of hydrogen effusion (i.e. H_2 bubbling) at the steel surface exposed to H_2S .

2.2 Corrosive medium

The support electrolyte contained $0.1 \text{ mol.L}^{-1} \text{ KClO}_4$. Chlorate ions are known to be large anions unable to adsorb on the steel surface. Continuous bubbling of acid gas was maintained during all experiments. Different gas mixtures were used, with 0.1 to 5 mol.% H_2S balanced with either N_2 or CO_2 .

pH was adjusted to 4.5 with addition of 1N potassium hydroxide (KOH) or 0.05N perchloric acid (HClO_4).

2.3 Permeation set up

Permeation measurements were performed using the electrochemical technique with a Devanathan-Stachurski type cell [10]. The experimental setup was made of twin cells separated with the steel membrane. They were equipped with double jacket in order to maintain the temperature at $21^\circ\text{C} \pm 2^\circ\text{C}$.

Unlike most papers dealing with hydrogen charging in H_2S environments, the charging face of the membrane was not maintained at the corrosion potential. Indeed, permeation transients are often strongly affected by the very fast precipitation of a FeS layer, which may hinder the potential impact of $\text{H}_2\text{S} / \text{CO}_2$ ratio. Therefore, a cathodic polarization was applied on the entry face similarly to Le Boucher experiments performed several decades ago [11]. At the beginning of the experiment the charging side of the membrane was immediately polarized at a low cathodic potential ($-1.5 \text{ V vs. Ag/AgCl}$). A potential scan was then performed at a slow rate (0.5 mV/min), up to the corrosion potential (E_{corr}). In order to check that this scan rate was sufficiently slow to ensure the steady-state, some tests were performed with a potentiostatic control with 100 mV steps. Each step was maintained until stabilization of both the cathodic current in the charging cell and the permeation current in the extraction cell. This procedure has a double advantage. First, it avoids as much as possible the rapid precipitation of a FeS layer at the steel surface. Then, it also allows applying a large range of cathodic current, simulating various charging conditions.

The exit surface of the membrane was held in a de-aerated $0.1 \text{ mol.L}^{-1} \text{ NaOH}$ solution and polarized at an anodic potential of 350mV vs. Hg/HgO reference electrode providing a direct measurement of the hydrogen flux crossing the steel membrane.

3 Results

3.1 Impact of CO_2 and H_2S on the cathodic current

The impact of CO_2 and H_2S on the cathodic current is illustrated on Figure 1 for tests performed under 0.1 to 5 mol.% H_2S gas balanced with N_2 or CO_2 .

The results obtained under potentiodynamic polarization (lines) are in good agreement with measurements obtained under potentiostatic control (points). They confirm that the potential scan rate is slow enough to ensure a quasi-steady-state behavior.

In the absence of CO₂, from E_{corr} to -1300mV vs. Ag/AgCl, an increase of H₂S partial pressure (P_{H₂S}) induces an increase of the cathodic current while for lower potentials, there is no effect. In the range of very low potentials, the cathodic current is then most likely due to the reduction of water. Close to E_{corr}, H₂S contribution to the cathodic current is assumed to be under diffusion control as reported in another paper [n°1124].

In the presence of CO₂, the cathodic current density increases for all P_{H₂S}. As a consequence, in the potential region close to E_{corr}, the effect of P_{H₂S} is less detectable and the different curves are very similar.

From these results, the following interpretation can be proposed for H⁺ contribution to the cathodic current close to E_{corr}. At E_{corr}, the proton reduction reaction is mainly under mass transfer control. The transport of acidity is mainly governed by the transport of the weak acid species, either CO₂ and/or H₂S. Indeed, at pH 4.5, H⁺ concentration is 3x10⁻⁵ mol.L⁻¹, while dissolved H₂S concentrations under 1, 9 and 50 mbar of H₂S are respectively 10⁻⁴, 9x10⁻⁴ and 5x10⁻³ mol.L⁻¹, thus at least 3 times higher than [H⁺]. For the experiments with CO₂, dissolved CO₂ concentration is close to 3.5x10⁻² mol.L⁻¹, thus representing the principal source of acidity.

A direct electroactive contribution of H₂S is also observed in Figure 1.a, and contributes to the observed increased cathodic current when P_{H₂S} increases. A more detailed characterization of this electrochemical contribution is proposed in another paper from the authors [n°1124].

Therefore, in our experimental conditions at pH 4.5, the interfacial concentration of H⁺ is mainly fixed by the weak acids. For tests performed under H₂S gas balanced with N₂, the cathodic current is then directly proportional to H₂S concentration. On the contrary, for the experiments with CO₂, the total concentration of weak acids is nearly constant whatever the P_{H₂S}, which is in good agreement with the trend of cathodic current measurements.

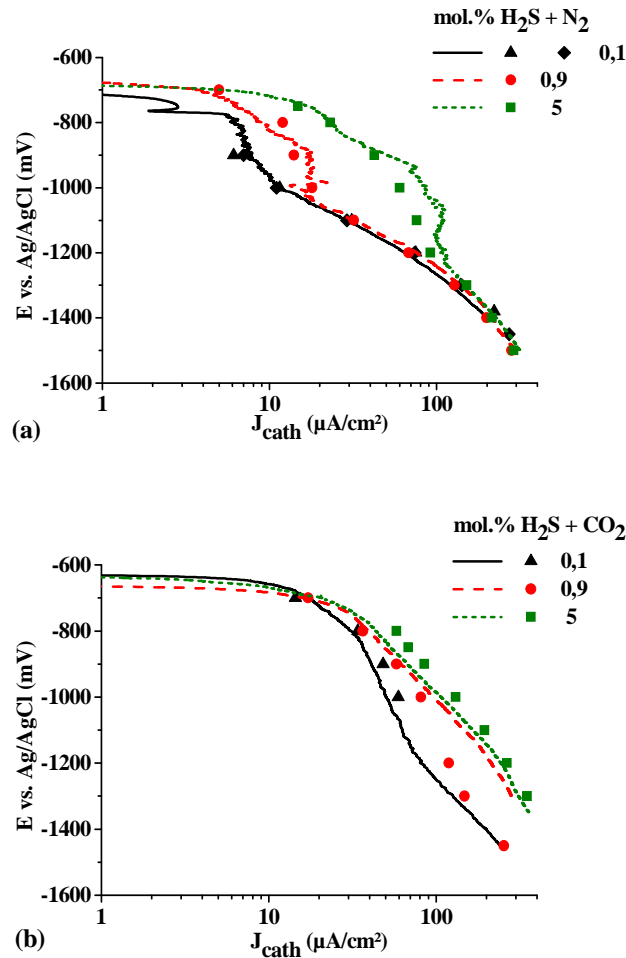


Figure 1: Applied potentials versus cathodic currents for various H₂S concentrations without CO₂ (a) and with CO₂ (b)

3.2 Impact of CO₂ and H₂S on the permeation current

The impact of CO₂ and H₂S on the permeation current is illustrated on Figure 2 for tests performed under 0.1 to 5 mol.% H₂S gas balanced with N₂ or CO₂. The general shape of the curves is similar to the one obtained by Le Boucher [11] (Figure 3) showing an increase of J_{perm} with J_{cath} at low cathodic overpotentials, followed by a decrease of J_{perm} for the very low potentials.

In the potential region close to E_{corr}, the permeation current shows similar variations with H₂S and CO₂ than the cathodic current. Indeed, without CO₂ in the gas mixture, H₂S partial pressure has a strong impact, inducing an increase of J_{perm}. On the contrary, in the presence of CO₂, for all P_{H₂S} the permeation current density is higher than in the absence of CO₂. Consequently the impact of H₂S on hydrogen charging is smoothed.

A comparison of the curves at iso-H₂S concentration suggests that the presence of CO₂ induces an increase of J_{perm} for potentials closed to E_{corr}.

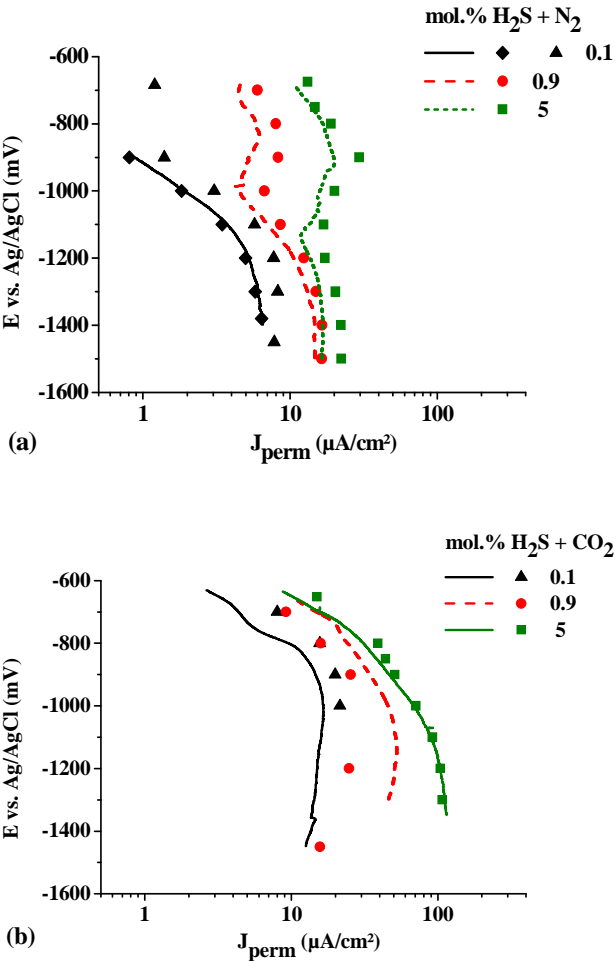


Figure 2: Applied potentials versus permeation currents for various H₂S concentrations without CO₂ (a) and with CO₂ (b)

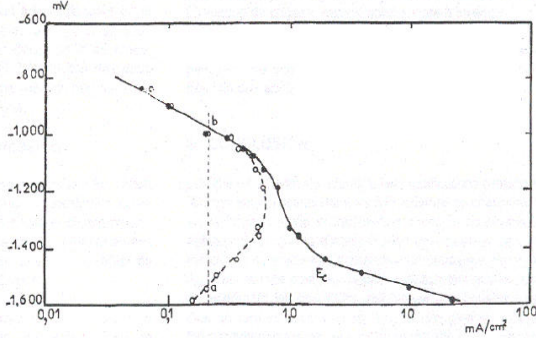


Figure 3: Relationship between permeation and cathodic polarization from [11]. 0.04mm-thick membrane exposed to 10 mM NaCl + 6.5x10⁻³ mol.L⁻¹ H₂S at pH 4.35 (O: permeation current, ●: cathodic current).

4 Discussion

The presence of 1 bar of CO₂ in the solution induces an increase of the cathodic current which impacts the permeation current in the same direction. Therefore the presence of CO₂ leads to an increase of the hydrogen charging in the steel. These results are highlighted by Figure 4 which represents the applied potential versus the permeation and the cathodic currents with and without CO₂.

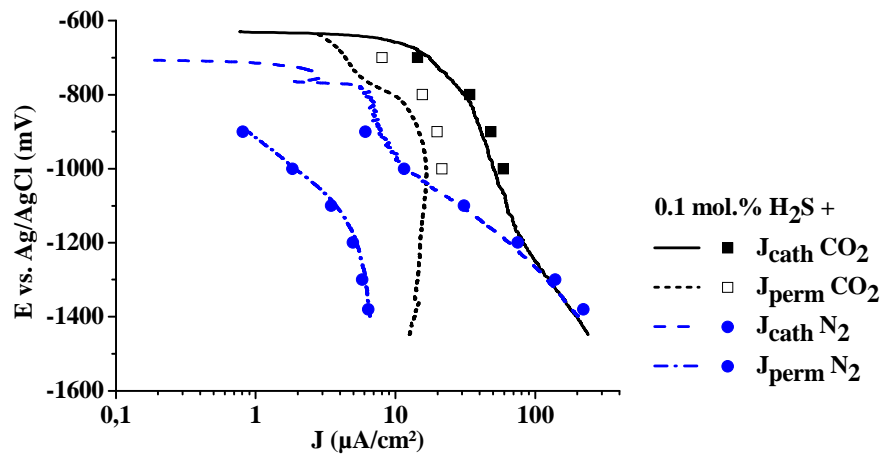


Figure 4: Comparison of the hydrogen charging and the cathodic currents under 1mbar H₂S with and without CO₂.

On Figure 5 (a) and (b), the global hydrogen permeation efficiency (E_g), defined as the ratio between J_{perm} and J_{cath} is plotted versus the applied potential and the applied current. These figures suggest that the increase of J_{perm} is not directly proportional to the increase of J_{cath} induced by the presence of CO₂ since E_g is higher with CO₂. Therefore, J_{cath} may not be the sole parameter controlling J_{perm} .

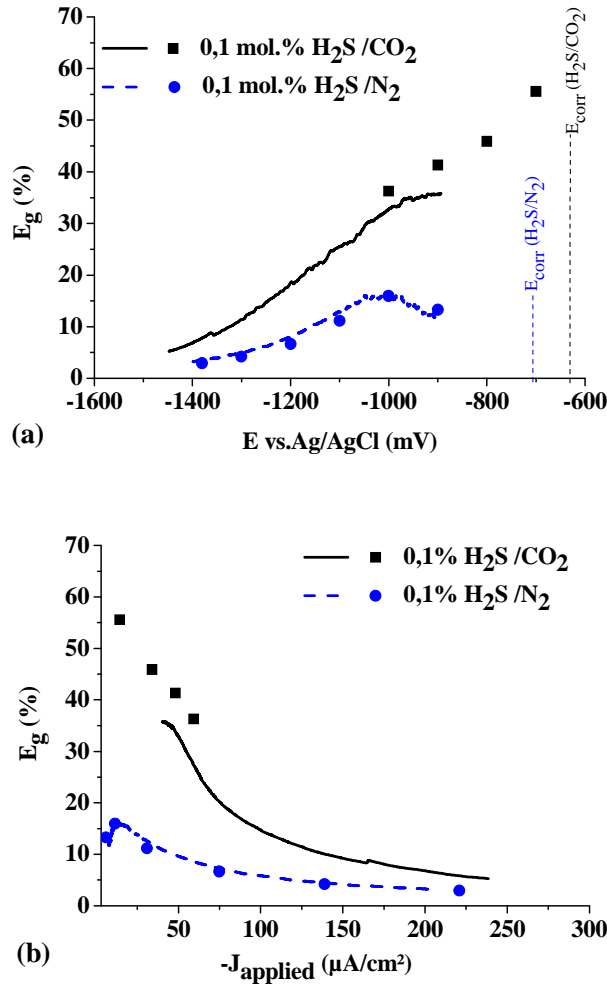


Figure 5: Global efficiency ($= J_{perm} / J_{cath}$) versus the applied potential (a) and versus the applied current (b) under 1mbar H_2S with and without CO_2 .

These results suggest that at a given pH and P_{H_2S} , the acidity added in the form of a weak acid buffer enhances hydrogen charging in the steel. In most situations, this weak acid is CO_2 or acetic acid, also used in NACE or EFC test solutions. For low pH applications, where P_{CO_2} in the field is supposedly high, the total reservoir of acidity of standard test conditions could rapidly underestimate the real field conditions; e.g. 1 bar CO_2 and 86 mM acetic acid of NACE A test solution contains the same amount of weak acid species than water in equilibrium with $P_{CO_2} = 4$ bar. Therefore any field pressure higher than 4 bar presents a higher oxidizing power than the standard test solution.

However, this discussion does not take into account the impact of corrosion scale precipitation. With high P_{H_2S} , a protective iron sulfide layer rapidly forms in field conditions, whereas standard test conditions with acetic acid or acetates tend to decrease the protectiveness of corrosion products. Standard test conditions should then still be more severe than field conditions.

However, with low $P_{\text{H}_2\text{S}}$, corrosion deposits might not be protective. This means that conditions where standard tests are less severe than in the field should not be overlooked.

Furthermore, the impact of corrosion product vanishes for stainless steels, where the main parameter is the oxidizing power. Then, any field condition with high P_{CO_2} might be underestimated with standard tests under 1 bar CO_2 and acetate buffer.

5 Conclusion

The impact of CO_2 on the cathodic current and the hydrogen charging in the steel was studied using a corrosive medium containing $0.1 \text{ mol.L}^{-1} \text{ KClO}_4$ maintained at pH 4.5. Under these conditions, under iso- $P_{\text{H}_2\text{S}}$, our experiments showed that the cathodic and the permeation currents are higher in the presence of CO_2 . This result is explained by the contribution of CO_2 which locally enhances H^+ availability at the steel surface, thus increasing the oxidizing power of the solution. As a consequence, with H_2S as hydrogen charging promoter, hydrogen permeation is increased when CO_2 is present.

Even though this work does not take surface films into account, the possible underestimation of the severity of low pH environments in tests performed at 1 bar total pressure remains to be studied.

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