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# Hydrogen charging in low alloy steels exposed to $H_2S$ : impact of $CO_2$ or $N_2$ in the gas mixture.

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#### Summary

This paper examines the influence of  $CO_2 / H_2S$  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  $H_2S$  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  $CO_2 / H_2S$  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<sup>-</sup> and HCO<sub>3</sub><sup>-</sup> 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 H<sub>2</sub>S concentrations with or without CO<sub>2</sub> 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 H<sub>2</sub>S 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  $H_2S$  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  $CO_2$  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  $CO_2$ . In other words, due to its ability to dissociate according to equations (a) and (b), the dissolved  $CO_2$  acts as a reservoir of additional protons available for the HER. As a consequence, carbon dioxide might influence the hydrogen charging in the steel.

$$H_2O + CO_2 \Leftrightarrow HCO_3^- + H^+$$
 (a)

$$HCO_3^- \Leftrightarrow CO_3^{2-} + H^+$$
 (b)

The presence of  $CO_2$  can also influence surface reactions [3]. Indeed bicarbonates produced by reaction (a) may eventually adsorb on the metal surface. Thus

depending on the CO<sub>2</sub> /  $H_2S$  ratio, a competition between HCO<sub>3</sub><sup>-</sup> and HS<sup>-</sup> 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  $P_{H2S}$ , 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  $P_{H2S} / P_{CO2}$  ratio on the X-axis instead of  $P_{H2S}$ . For experiments under 1 bar total pressure, the range of  $P_{H2S} / P_{CO2}$  varies from nearly zero (low  $P_{H2S}$  and  $P_{CO2}$  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  $CO_2$  /  $H_2S$  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 cm<sup>2</sup>. Before each experiment, both faces of the membrane were manually polished to grade 2500 and cleaned in acetone and ethanol using a 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 mol.L<sup>-1</sup> KClO<sub>4</sub>. 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<sub>4</sub>).

#### 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  $21^{\circ}$  +/-  $2^{\circ}$ .

Unlike most papers dealing with hydrogen charging in H<sub>2</sub>S 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  $H_2S / CO_2$  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 V vs. Ag/AgCl). A potential scan was then performed at a slow rate (0.5 mV/min), up to the corrosion potential (E<sub>corr</sub>). 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 mol.L<sup>-1</sup> 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<sub>2</sub> and H<sub>2</sub>S 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 CO<sub>2</sub>, from E<sub>corr</sub> to -1300mV vs. Ag/AgCl, an increase of H<sub>2</sub>S partial pressure (P<sub>H2S</sub>) 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<sub>corr</sub>, H<sub>2</sub>S contribution to the cathodic current is assumed to be under diffusion control as reported in another paper [n<sup>°</sup>124].

In the presence of CO<sub>2</sub>, 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<sup>+</sup> 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 CO<sub>2</sub> and/or H<sub>2</sub>S. Indeed, at pH 4.5, H<sup>+</sup> concentration is  $3x10^{-5}$  mol.L<sup>-1</sup>, while dissolved H<sub>2</sub>S concentrations under 1, 9 and 50 mbar of H<sub>2</sub>S are respectively  $10^{-4}$ ,  $9x10^{-4}$  and  $5x10^{-3}$  mol.L<sup>-1</sup>, thus at least 3 times higher than [H<sup>+</sup>]. For the experiments with CO<sub>2</sub>, dissolved CO<sub>2</sub> concentration is close to  $3.5x10^{-2}$  mol.L<sup>-1</sup>, thus representing the principal source of acidity.

A direct electroactive contribution of  $H_2S$  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<sup>9</sup>124].

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 H<sub>2</sub>S gas balanced with N<sub>2</sub>, the cathodic current is then directly proportional to H<sub>2</sub>S concentration. On the contrary, for the experiments with CO<sub>2</sub>, the total concentration of weak acids is nearly constant whatever the P<sub>H2S</sub>, which is in good agreement with the trend of cathodic current measurements.



Figure 1: Applied potentials versus cathodic currents for various  $H_2S$  concentrations without  $CO_2$  (a) and with  $CO_2$  (b)

#### 3.2 Impact of CO<sub>2</sub> and H<sub>2</sub>S on the permeation current

The impact of  $CO_2$  and  $H_2S$  on the permeation current is illustrated on Figure 2 for tests performed under 0.1 to 5 mol.%  $H_2S$  gas balanced with  $N_2$  or  $CO_2$ . 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  $H_2S$  and  $CO_2$  than the cathodic current. Indeed, without  $CO_2$  in the gas mixture,  $H_2S$  partial pressure has a strong impact, inducing an increase of  $J_{perm}$ . On the contrary, in the presence of  $CO_2$ , for all  $P_{H2S}$  the permeation current density is higher than in the absence of  $CO_2$ . Consequently the impact of  $H_2S$  on hydrogen charging is smoothed.

A comparison of the curves at iso- $H_2S$  concentration suggests that the presence of  $CO_2$  induces an increase of  $J_{perm}$  for potentials closed to  $E_{corr}$ .



Figure 2: Applied potentials versus permeation currents for various  $H_2S$  concentrations without  $CO_2$ (a) and with  $CO_2$  (b)



**Figure 3:** Relationship between permeation and cathodic polarization from [11]. 0.04mm-thick membrane exposed to 10 mM NaCl +  $6.5 \times 10^{-3}$  mol.L<sup>-1</sup> H<sub>2</sub>S at pH 4.35 (O: permeation current,  $\bullet$ : cathodic current).

#### 4 Discussion

The presence of 1 bar of  $CO_2$  in the solution induces an increase of the cathodic current which impacts the permeation current in the same direction. Therefore the presence of  $CO_2$  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  $CO_2$ .



Figure 4: Comparison of the hydrogen charging and the cathodic currents under 1mbar  $H_2S$  with and without  $CO_2$ .

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  $CO_2$  since  $E_g$  is higher with  $CO_2$ . 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  $P_{H2S}$ , 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<sub>2</sub> or acetic acid, also used in NACE or EFC test solutions. For low pH applications, where  $P_{CO2}$  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<sub>2</sub> and 86 mM acetic acid of NACE A test solution contains the same amount of weak acid species than water in equilibrium with  $P_{CO2} = 4$  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  $P_{H2S}$ , 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  $P_{H2S}$ , 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  $P_{CO2}$  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 mol.L<sup>-1</sup> KCIO<sub>4</sub> maintained at pH 4.5. Under these conditions, under iso-P<sub>H2S</sub>, 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<sup>+</sup> availability at the steel surface, thus increasing the oxidizing power of the solution. As a consequence, with H<sub>2</sub>S 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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