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Corrosion of Pure iron and Hydrogen Permeation in the Presence of H₂S with O₂ contamination

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ABSTRACT

This paper examines the influence of traces of oxygen on corrosion and hydrogen charging of steel in an H₂S containing environment. It is well known that H₂S promotes hydrogen entry into steels, that may result in many types of steel failures such as Hydrogen Induced Cracking (HIC), Sulfide Stress Cracking (SSC), and Stress-Oriented Hydrogen Induced Cracking (SOHIC). Since it is a huge concern for oil and gas industries, standard test methods have been developed and published as NACE technical methods (e.g. NACE TM0284 and NACE TM0177). Though it is recognized that oxygen pollution should be avoided during H₂S cracking tests, there is still a lack of experimental data to illustrate the potential impacts of a small oxygen pollution.

The aim of the present study is to check if oxygen traces can modify the mechanisms of corrosion and hydrogen charging of steel in H₂S containing medium. Experiments consisted of hydrogen permeation measurements through a thin pure iron membrane. They were performed at free potential circuit in order to ensure more realistic environmental conditions. The corrosion rate was also evaluated and test solutions analyzed.

Key words: H₂S, O₂, HIC, SSC, hydrogen permeation, hydrogen embrittlement.

INTRODUCTION

Materials used in oil and gas industries can be exposed to sour environments containing hydrogen sulfide (H_2S), which is corrosive and known to promote hydrogen entry into steels. This may lead to several types of steel failures such as Hydrogen Induced Cracking (HIC), Sulfide Stress Cracking (SSC), and Stress-Oriented Hydrogen Induced Cracking (SOHIC).

Corrosion and hydrogen embrittlement of steels in H_2S containing environments has been studied for several decades. Standard test methods have been developed for the selection and the qualification of steels for use in H_2S containing environments, such as NACE TM 0177 and TM 0284.^{1,2} These standards strongly recommend to avoid oxygen infiltration in test environments. For instance, it is stated that *'obtaining and maintaining an environment with minimum dissolved O_2 contamination is considered very important'*. It is also mentioned that O_2 contamination may induce an increase of the corrosion rate and reduce hydrogen evolution and hydrogen entry into the steel. However, it is also recognized that *'systematic studies of the parameters affecting these phenomena have not been reported in the literature'*.

There are many different ways by which oxygen can pollute a test medium such as, a poor deaeration of the initial test solution, poor sealing of test reactors, the use of plastic tubing permeable to oxygen, and diverse other operations during the test (solution sampling, pH adjustment, etc.). For the present study, we were interested in investigating the impact of a continuous ingress of small amounts of O_2 in a test vessel during a corrosion test with H_2S .

It has been shown by Song et al.,³ that a solution continuously bubbled with a mixture of H_2S and O_2 , acidifies continuously and does not rise back to neutrality after H_2S purging with inert gas (argon, nitrogen). This experimental finding is in good agreement with the reaction pathway proposed by Crolet and Pourbaix⁴, showing that O_2 and H_2S can react to form thiosulfate or tetrathionate. In both cases, H^+ ions are also produced, resulting in a decrease in pH. The produced S-O compounds can then modify the kinetics and corrosion mechanisms.

It is also well-known that H_2S promotes hydrogen entry in steels via sulfur adsorbates.⁵⁻⁷ Surface reactions with oxygen or with $\text{O}_2 - \text{H}_2\text{S}$ reaction products could interact with the hydrogen entry process. Some authors have proposed to use thiosulfate solutions to replace H_2S in cracking experiments.^{8,9} Indeed, they found that thiosulfate reduction at the metal surface could result in the formation of H_2S , resulting in an increase of hydrogen permeation.

In summary, oxygen traces in H_2S containing environment could then modify the system in three distinct areas by:

- changing the composition of the corrosive environment;
- modifying the corrosion rate and the nature of corrosion deposits;
- interacting with H_2S adsorbates and changing the efficiency of hydrogen entry.

This paper aims at improving the understanding of corrosion mechanisms and hydrogen entry into steels in H₂S containing environment polluted by traces of oxygen. Typical experiments consist in exposing iron coupons in saline water saturated with H₂S and with a continuous and well controlled O₂ entry. Chemical analysis of the test solution is performed in order to identify reaction products between O₂ and H₂S.

Electrochemical measurements are also carried out on pure iron membranes to evaluate the effect of O₂ on corrosion and on hydrogen entry in the metal.

EXPERIMENTAL PROCEDURE

Control of oxygen in test media

In order to control the quantity of oxygen introduced in the test cell, two separate gas lines with mass flow controllers (MFC's) were used. The first gas line consists in pure H₂S or H₂S/N₂ mix, with a typical flow-rate of 17 to 20 mL/min. The second gas line is fed with O₂/N₂ at a typical O₂ concentration of 10 %, and is used at a flow-rate comprised between 0 and 3 mL/min. Gas lines are made of 316L stainless steel and several valves are used to manage the gas supply into the cell. Gases are homogenized in a spiral gas line of about 1 meter before bubbling into the test solution and the oxygen content in the gas line immediately before entering into the test cell is checked with a HACH 410 Orbisphere™ probe. With this system, O₂ partial pressure in the gas entering into the test cell can then be controlled precisely between 0 and a few tens of mbar.

The theoretical amount of dissolved oxygen content of the test solution is related to the oxygen partial pressure in the gas phase. Indeed, the dissolved oxygen content follows Henry's law, which shows a linear dependence between the concentration of a dissolved gas in a given solution and its content in the gas phase in equilibrium. According to Henry's law:

$$C_i = K_{Hi} P_i \quad \text{Equation 1}$$

where C_i is the dissolved gas concentration, K_{Hi} is the Henry's constant of gas i , and P_i is the gas partial pressure. The Henry's constant values for H₂S and O₂ at 25°C and 1 atm are respectively 0.1 mol/L/bar and 1.3×10^{-3} mol/L/bar.^{4,10-12} The range of P_{O_2} comprised between 0 and a few tens of mbar thus corresponds approximately to 0 – 500 ppb mass. dissolved O₂ at saturation. Since the recent revisions of NACE TM0177 and NACE TM0284 mention some O₂ limits expressed in mass ppb, this unit will be used in the paper, though the parameter that was indeed controlled was O₂ partial pressure.

Corrosive medium

In order to keep the system as simple as possible and to avoid interferences with other chemicals, most tests were carried out solutions containing 35 g/L NaCl without added acids or buffering species. This solution is called “Model solution without buffer”. Continuous bubbling of gases was maintained during all experiments. Two gas compositions were tested: pure H₂S and a mixture of H₂S (87.5%), N₂ (11.25%) and O₂ (1.25% corresponding to 500 mass. ppb dissolved O₂). In addition, comparative tests were carried out on the NACE A solution (5% NaCl, 0.5 % acetic acid), with the same gas mixtures.

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 by the steel membrane. They were equipped with double jacket in order to maintain the temperature at 24 +/- 2 °C. However, the double jacket did not cover the area at the vicinity of the membrane, and temperature variations close to the membrane might have been slightly higher than +/- 2 °C. Day – night variations in the laboratory at the time of the experiments were in the order of +/- 4 °C, and these fluctuations had an impact on some permeation measurements, e.g. those presented on Figure 10. The membrane consisted in pure iron, with the exit face covered by palladium following well established procedures.¹³ The membrane thickness was 0.5 mm and the exposed surface was 16 cm². Under such conditions of thickness and environment, it is considered that permeation is mostly governed by reactions at the entry face, minimizing the impact of bulk diffusion of hydrogen.^{6,7,14,15} The charging side of the membrane was left at free potential in order to be representative of standard qualification tests. The exit surface of the membrane was held in a deoxygenated 0.1 mol.L⁻¹ NaOH solution and polarized at an anodic potential of 250 mV vs. Hg/HgO (1M KOH) reference electrode providing a direct measurement of the hydrogen flux across the steel membrane.

In addition to the permeation membrane, weight-loss specimens (0.9 cm x 0.9 cm x 0.05 cm) were also introduced into the charging cell. These coupons were used for weight-loss corrosion rate evaluation, as well as surface analysis by Scanning Electronic Microscopy (SEM), and X-Ray Diffraction (XRD).

Considering the permeation membrane and iron coupons, the ratio between test solution volume and exposed surface was close to 20 mL/cm².

During each test, the charging solution was periodically sampled and analyzed by ionic chromatography (IC) to determine the sulfur–oxygen (S-O) species concentrations. The total volume of solution sampled represents less than 20 mL compared to 400 mL in total. No replenishment was thus necessary.

At the end of the test, the total sulfur content in the charging solution was analyzed by Inductively Coupled Plasma Emission Spectroscopy (ICPES).

Tested material

Permeation membranes were machined in pure iron (chemical composition given in Table 1) and consisted in thin discs of 57 mm diameter and 0.5 mm thickness, with a tongue of 7 x 7 mm used for electrical connection. In order to reduce metallurgical defects such as dislocations, the permeation membranes were heat treated under vacuum at 900 °C for 30 minutes.

Table 1 : Chemical composition of test material (mass. ppm)

Al	Cr	Cu	Mn	Ni	Si	Ti	C	P	S	Fe
107	133	55	240	159	100	5	18	60	48	Bal

RESULTS

Calibration and measurement of oxygen concentration

Preliminary tests were performed using CO₂ instead of H₂S in the acid gas line, and N₂/O₂ in the oxygen line, in order to check that dissolved O₂ could be controlled at various levels between a few tens of ppb and 500 ppb. Such verification could not be performed with H₂S, since reactions between O₂ and H₂S are expected, resulting in free O₂ concentration much below its solubility equilibrium. Different levels of O₂ partial pressure were then obtained by selecting different flow rates for both gas lines. Dissolved O₂ concentration was measured with the O₂ probe, and compared with theoretical value at equilibrium. The results illustrated in Figure 1 show that stable O₂ content can easily be achieved. Experimental values were very close to theoretical values calculated from mass flow-rates settings and Henry's law, also shown on Figure 1.

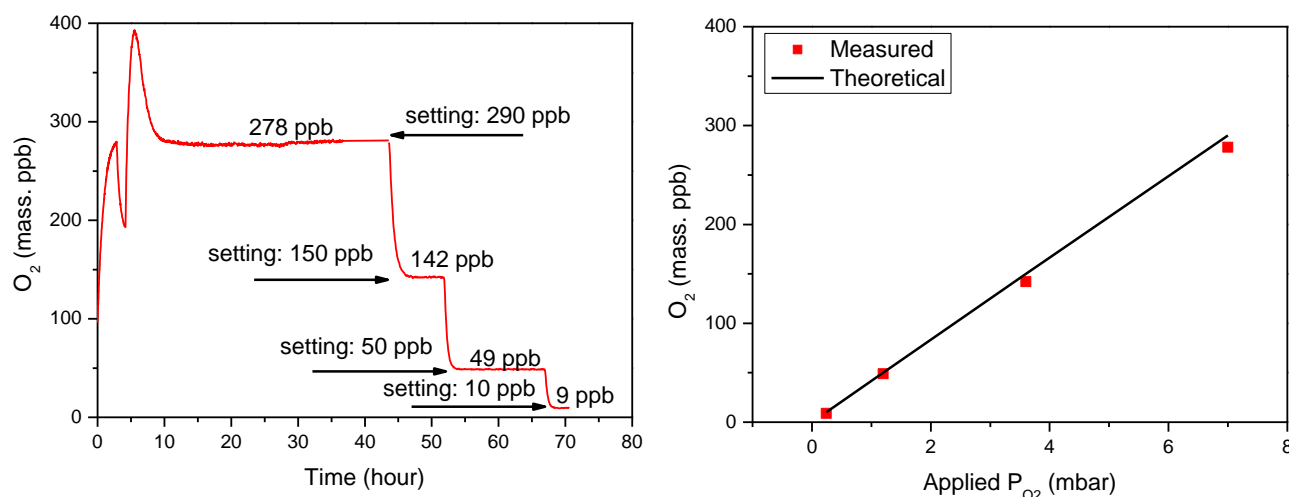


Figure 1: Verification of O₂ control at various levels in the test medium and comparison with setting values

It could be concluded from these tests that our gas mixing system allowed to control oxygen content at least up to 13 mbar, corresponding to approximately 500 ppb dissolved O₂. This system was then used

with H_2S . No additional O_2 measurements were performed with H_2S , since $\text{O}_2 - \text{H}_2\text{S}$ reaction was likely to occur quickly in water. In addition, H_2S could also deteriorate the oxygen probe. It was also carefully checked that for the reference tests without oxygen, the residual O_2 concentration was well controlled below 5 ppb. As a consequence, test conditions with O_2 pollution correspond to a well-controlled PO_2 in the gas phase bubbling into the test solution, but the effective value of dissolved O_2 is not known, due to $\text{H}_2\text{S} - \text{O}_2$ reactions. One must then keep in mind that O_2 values in mass ppb given in this paper thus correspond to what would be observed in the test solution in the absence of reactive species (e.g. H_2S , but also dissolved iron that can precipitate with O_2). The same remark holds for NACE TM0284 and NACE TM0177, where maximum O_2 content in mass. ppb is specified.

Impact of oxygen on corrosive medium

Model solution without buffer

In order to determine the impact of O_2 contamination on the test solution, several permeation tests were conducted with continuous pH measurement and periodic sampling of test solutions used for chemical analysis. The pH trends of test solutions with or without oxygen are shown in Figure 2. These pH measurements were performed during a permeation experiment, i.e. with iron coupons in the test solution.

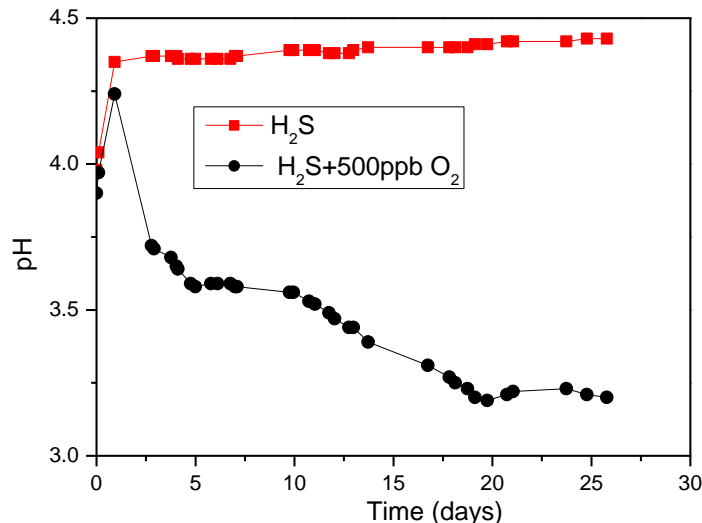
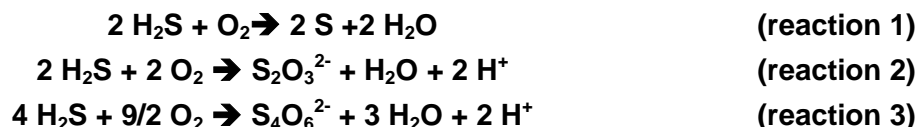


Figure 2: pH evolution of a corrosion test solution composed of 35 g/L NaCl with 1 bar H_2S . Impact of 500 ppb O_2 continuous contamination.

In the beginning of both tests, pH is close to 3.9, corresponding to H_2S saturated water at 1 bar. As expected, pH then increases up to 4.3, corresponding to FeS saturation. Once saturation is reached, no change of pH is observed for the test without O_2 . On the contrary the test solution treated with both H_2S

and O₂ shows a continuous decrease of pH until the end of the test. After 1 month exposure, the pH has decreased by more than 1 pH unit. At the end of the test, the oxygen free solution has a pH value of 4.4 and the solution treated with both H₂S and O₂ has a pH value of 3.2.

This result illustrates that during the first hours of the test in both solutions, the major reaction is the corrosion of iron which produces alkalinity and dissolved iron and consequently increases the pH. Once iron sulfide saturation is reached, the pH stops increasing. However, in the test solution exposed to O₂ pollution, there are additional reactions between oxygen and H₂S producing S-O species which acidify the medium. This is in agreement with Song and Crolet works, who proposed the following reactions:^{3,4}



Over a long time period this cumulative acidification can have a considerable effect on the pH of the solution.

In addition to in situ pH measurements, periodic sampling of the test solutions was performed for chemical analysis. The main results are plotted on Figure 3. Before analysis by ionic chromatography, residual dissolved H₂S was eliminated by argon stripping in the water aliquot. The main dissolved sulfur compound detected was sulfate.

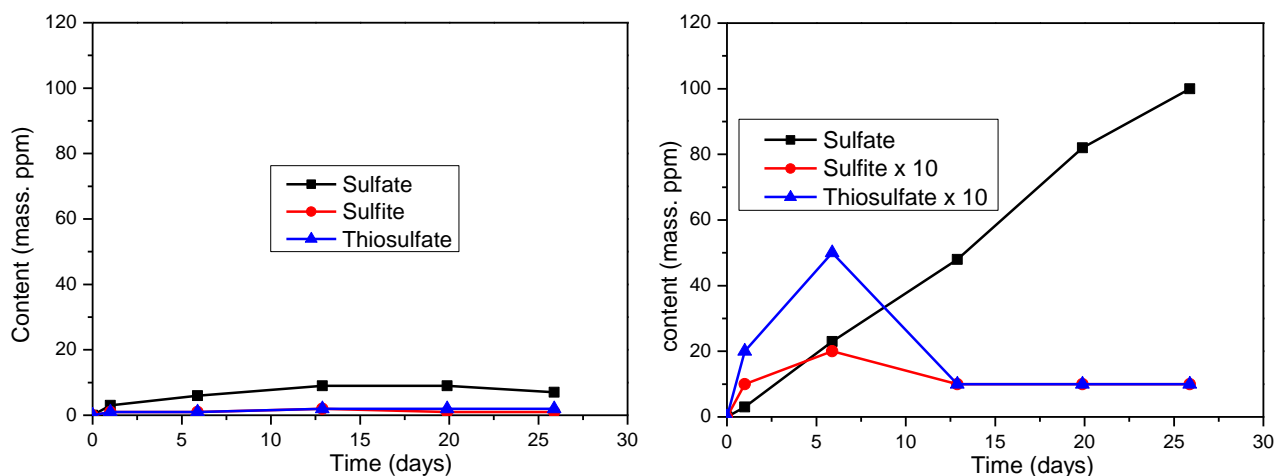


Figure 3: Chemical analysis by ionic chromatography of S-O species in test solutions composed of 35 g/L NaCl with 1 bar H₂S, without (a) and with (b) continuous O₂ contamination at 500 ppb

In the test solution with oxygen, the sulfate concentration increases gradually and reaches 100 mg/L at the end of the test, after 4 weeks exposure. Sulfites and thiosulfates are also detected at trace levels. A yellowish elemental sulfur deposit was also observed in the corresponding test cell. These results are in good agreement with reactions 1 – 3 proposed by Crolet and Song.^{3,4} According to these reactions,

thiosulfate is expected, however it is known that it is unstable and can easily be oxidized to sulfate and elemental sulfur in an oxygen containing environment. ICPES results showed that solution treated with oxygen, consisted of 45 ppm of total sulfur. Hence, sulfur compounds detected by ionic chromatography represent around 70% of dissolved sulfur. On the contrary tests conducted without added oxygen did not show any elemental sulfur precipitation and no significant increase of sulfate, sulfite or thiosulfate content.

At the end of the test, the dissolved iron content for the oxygen-free test is about 0.35 mg/L and about 37.6 mg/L for the test in the presence of oxygen. This higher value of the dissolved iron content in the presence of oxygen is probably due to the acidification of the solution which increases the solubility of iron. At the same time bulk precipitation consisting mainly of elemental sulfur was also observed.

Test in NACE A solution

In addition to the tests in model solutions, a few experiments were also performed in standard NACE A solution. This solution is used for testing sour resistant materials, and is composed of 5 % NaCl and 0.5 % acetic acid, saturated under 1 bar H_2S . As for the tests in model solution, the ratio between the test solution volume and the metal surface was 20 mL/cm². pH evolutions during these tests are illustrated in Figure 4.

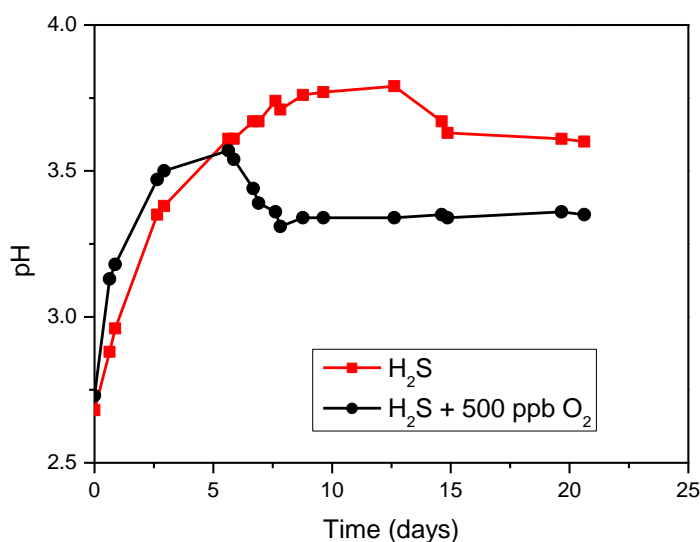


Figure 4: pH evolution of a corrosion test in NACE A solution with 1 bar H_2S . Impact of 500 ppb O_2 continuous contamination

The initial pH for tests in NACE A solution is about 2.7 in conditions with and without oxygen. As for the tests in 35 g/L NaCl, an increase in pH in both tests was observed at the beginning of the test, due to the production of alkalinity associated with the corrosion reactions. For the test solution without O_2 pollution, pH slowly increased up to 3.8 after 200 hours. Then it stayed stable, or decreased slowly to 3.6 after 300 hours. For the test with O_2 pollution, pH increase was slightly less pronounced, with a

maximum value of 3.6 reached after 50 hours. Then a decrease by 0.3 pH units is observed and a stabilized value around 3.3 – 3.4 is observed between 200 hours and until the end of the test. This pH stability of the test solutions, especially for the solution with oxygen ingress, is probably related to the buffer effect of acetic acid.

The dissolved iron content at the end of the test for the solution with and without oxygen is 185 and 179 mg/L, respectively. These high values compared to the values observed for the NaCl solution (35 g/L) are, as already mentioned in the preceding paragraph, due to the high acidity of the solutions which enhanced cathodic reaction (proton reduction) and by the way limits the precipitation of iron sulfides and / or iron oxides.

Impact of oxygen on corrosion rate and corrosion products

The results showing the effect of oxygen on corrosion rate are presented in Figure 5. Four series of tests were performed in parallel, with and without oxygen in 35g/L NaCl solution, and one series in NACE A solution.

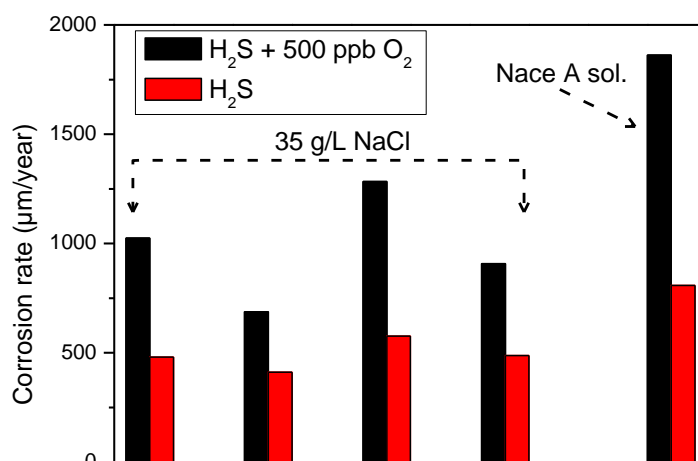


Figure 5: Comparison of corrosion rates for several tests with and without oxygen pollution

Model solution without buffer

As expected, oxygen pollution results in a strong increase in the corrosion rate, by a factor of 2, compared to experiments carried out without oxygen. This increase in corrosion rate can be associated with the continuous decrease of pH due to $O_2 - H_2S$ reactions. It is also possible that thiosulfate, or other unstable S-O species that may have formed, contribute directly to the cathodic current density and then increase the corrosion rate.

Surface analysis of the coupons was also performed. Results of XRD analysis showed that mackinawite was dominant, with also traces of greigite. No iron oxides or hydroxides were detected for

the tests with O₂ pollution. Although XRD analysis did not allow distinguishing differences between scale composition formed at the iron surface, SEM observations did (Figure 6). For oxygen-free tests, a rather homogeneous surface is observed, mainly composed of iron and sulfur as shown by Electron-Dispersive Spectroscopy (EDS) cartography. On the other hand, for the test in the presence of oxygen, the EDS cartography shows differences in the deposits with zones rich in oxygen and others rich in sulfur. In addition, in the tests carried out in the presence of oxygen, a huge amount of precipitates was also observed on the walls of the test cells. XRD analysis was also performed, and these deposits consisted mainly of elemental sulfur and marcasite.

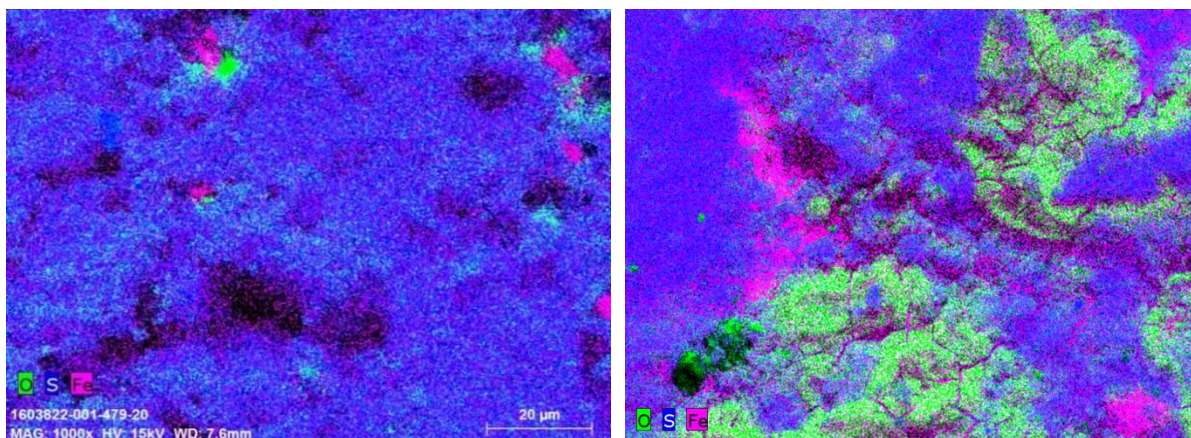


Figure 6 : EDS mapping for corrosion products at the metal surface after tests (a) without oxygen (b) with oxygen (same magnification for both pictures)

Test in NACE A solution

For the tests performed in NACE A solution, O₂ also enhances the test solution severity. The corrosion rate is close to 2 mm/year after 1 month in this test solution when O₂ is added, while it is a bit less than 1 mm/year in O₂-free conditions. The ratio is in the same order as that previously observed in non-buffered 35 g/L NaCl solution. In general, it is observed that the corrosion rate is approximately twice as great in the NACE A solution as in the model solution (NaCl 35 g/L), for the same gas mixture. This difference is probably related to the lower pH of the NACE A solution, which in addition to promoting the cathodic reaction (proton reduction), also limits the formation of the corrosion deposit layer. However, contrary to the tests in non-buffered solutions, this increase of corrosion rate cannot be attributed to a large change of pH. A direct contribution of H₂S-O₂ reaction products is thus more likely. As already mentioned, such species can provide a direct electrochemical reactivity. They may also interfere with test solution chemistry at the surface, where the pH may vary significantly from the bulk pH.

As for the test of the model solution treated with oxygen, a large deposit is observed on the cell wall of the test treated with oxygen. XRD analysis of the powder shows that it is mainly composed of iron sulphides (pyrite, marcasite, pyrrhotite) and elemental sulfur (Figure 7).

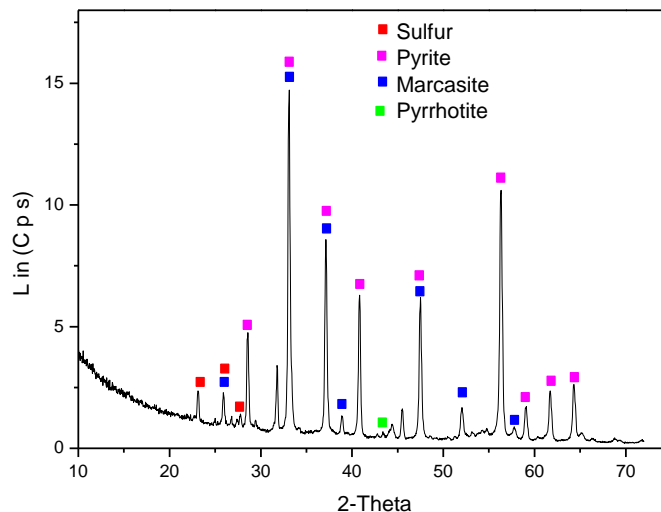


Figure 7: XRD characterization of deposit sampled at the walls of the cell after permeation test in NACE A solution with oxygen contamination

Impact of corrosion on hydrogen permeation

Reproducibility of permeation measurements

In order to verify the reproducibility of electrochemical permeation measurements, 5 series of tests were carried out in the model solution without buffer (35 g/L NaCl solution) under 1 bar H_2S . The results obtained are shown in Figure 8. It is observed on permeation transients that after 40 h of test, permeation current densities of between 41 and 48 $\mu A/cm^2$ are obtained, i.e. a dispersion of less than 10%.

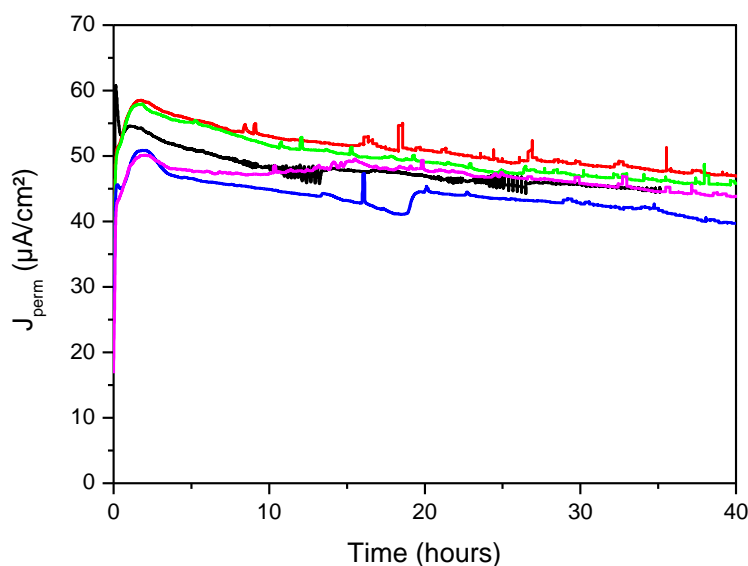


Figure 8: Reproducibility of permeation measurements in 35 g/L NaCl solution under 1 bar H_2S

Model solution without buffer

The effects of oxygen on permeation through a pure iron membrane in NaCl saturated solution with 1 bar H_2S are illustrated in Figure 9. It must be noted that impedance measurements of the entry face were performed periodically during all the test, leading to small fluctuations of the permeation current. This explains the visual impression of noise on these permeation transients. No particular effect of oxygen is observed on the permeation current during the first hundred hours of the test. However, after 200 h, a linear decrease in the hydrogen permeation current is observed in the presence of O_2 . After 25 days of tests, the permeation current density was about 39 and 19 $\mu\text{A}/\text{cm}^2$ respectively in the solution without oxygen and in the solution treated with oxygen. This trend is reproducible for the four sets of tests that have been done under these conditions.

This decrease of permeation current is somewhat unexpected, since it was observed that in oxygen treated solution, the pH decreases with time down to 3.2, while it stayed close to 4.4 without O_2 pollution. Indeed, increasing the acidity should normally have the opposite effect, with an increase of permeation rate.¹⁶

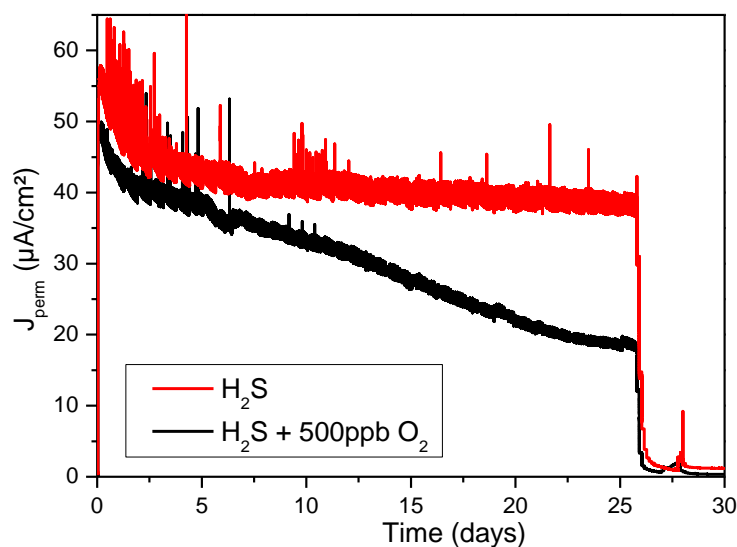
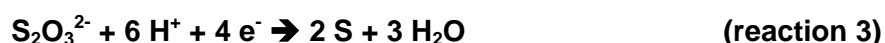


Figure 9: Permeation curves in 35g/L NaCl under 1 bar H_2S , with and without oxygen

Comparing corrosion and permeation rates also gives an interesting perspective. The weight-loss corrosion for the tests conducted without O_2 is 490 $\mu\text{m}/\text{year}$, corresponding to an average corrosion current density of 42 $\mu\text{A}/\text{cm}^2$. For the same set of tests, the average permeation rate was 41 $\mu\text{A}/\text{cm}^2$, i.e. exactly the same as the corrosion rate. This result is a clear evidence that the cathodic reaction involved in pure H_2S systems consists only of proton reduction, and also that the permeation efficiency is 100 %, meaning that 100 % of hydrogen produced by the cathodic reaction has entered into the steel. This type of behavior is typical in such systems, providing that no diffusion limitation takes place, which requires that the membrane thickness is sufficiently thin.^{6,7,14,15} On the contrary for the tests with

O₂ pollution, the average corrosion current density was 83 µA/cm², while the average permeation rate was only 30 µA/cm². In that case, the apparent efficiency is decreased to 35 %.

The decreasing flux of hydrogen through the iron membrane in presence of O₂ is not yet fully understood. It could be interpreted as an effect of corrosion products which blocks the iron membrane surface. It may be emphasized that the quantity of precipitates, as determined by visual observations, was significantly higher for the test in presence of O₂. However, it must be noted that tests with O₂ also resulted in doubling the corrosion rate. If a global blocking effect was at the origin of the decrease of hydrogen permeation, it would be expected that a similar consequence on the corrosion rate would take place, however this has not been observed. Oxygen or more likely reaction products between O₂ and H₂S probably have a significant contribution to cathodic reactions. Indeed, thiosulfates have been identified in the literature¹⁷ as a candidate reaction product, possibly leading to the following electrochemical contribution:



At this stage, the most likely cause to explain the decrease of permeation rate is a decrease of hydrogen entry promotion at the metal surface. Considering that hydrogen entry is promoted by specific adsorbates that play the role of intermediate reaction site for proton reduction,¹⁸ those formed in presence of O₂ may be less efficient than those observed in pure H₂S media. A theoretical analysis proposed by Marcus and Protopopoff¹⁹ compared the adsorption of oxygen or sulfur atoms on iron, in various environments containing H₂S and thiosulfates. According to these authors, the presence of thiosulfate could modify the ratio between O_{ads} and S_{ads}, with potential consequences on the anodic reaction and on the enhancement of H entry into the metal.

Test in NACE A solution

As in the model solution, a higher permeation current density peak is observed in the absence of oxygen (Figure 10). However, the permeation current density evolves very rapidly in both cases to the same value (around 40 µA/cm²), unlike the tests on the model solution which showed a continuous gap between the two permeation transients. Apparently, the impact of O₂ is much less pronounced than previously observed in non-buffered solution. It is likely that acetic acid masks the contribution of O₂ – H₂S reaction products on the cathodic reactions. In addition, it also has a strong influence of surface depositis (precipitation of corrosion products and adsorption reactions), thus minimizing the influence of O₂ at the surface. Still, it must be recalled that the corrosion rate was doubled for the test with O₂, showing again that the apparent permeation efficiency was decreased.

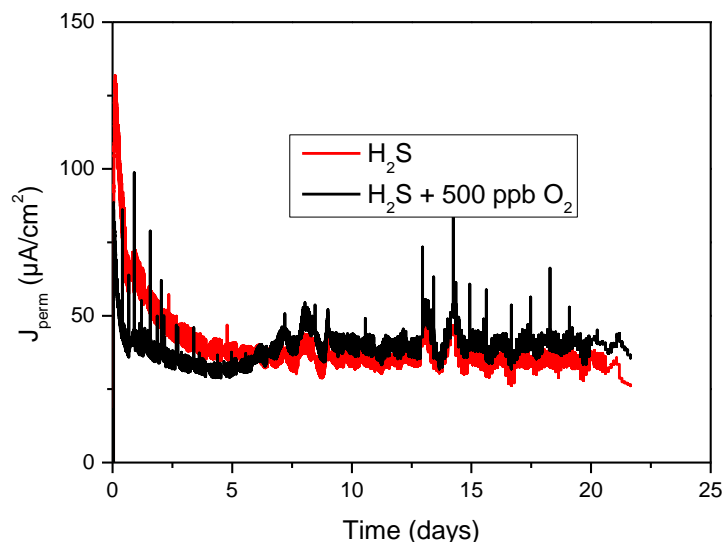


Figure 10: Permeation curves in NACE A solution under 1 bar H_2S , with and without oxygen

CONCLUSIONS AND FUTURE WORK

The effect of oxygen traces on pure iron corrosion and hydrogen permeation was studied in a model aqueous NaCl (35g/L) and NACE A solution under 1bar H_2S at ambient temperature with and without O_2 content corresponding to 500 ppb (13 mbar).

It has been observed that in the presence of oxygen, it reacts with H_2S and predominantly produces dissolved sulfates and precipitation of elemental sulfur. Sulfite and thiosulfate are also detected, and are probably unstable intermediate species, which may also react with the steel before to reach the more stable sulfate form. As expected, the reaction paths lead to a strong acidification of the test medium, with an amplitude of one pH unit in one month.

Corrosion is strongly accelerated in the presence of O_2 , by a factor of about 2 under given conditions. Differences are also observed in the morphology and homogeneity of corrosion deposits, with more oxides and elemental sulfur present in the case of O_2 polluted systems. In addition, in both cases (with and without O_2), XRD analyzes show mackinawite as the majority compound. Test solution acidification is thought to be the major reason for enhancing the corrosion rate. However, a similar increase was also observed in NACE A solution, where the impact of O_2 on pH was less visible due to pH stabilization by acetates. It is thus likely that the other O_2 - H_2S reaction products also play a role in increasing the corrosivity, e.g. by providing a direct electrochemical reactivity, or by modifying the protectivity of the corrosion products formed at the metal surface.

In model solution containing only NaCl, it is also observed that the permeation current density continuously decreases in the presence of oxygen, which is rather surprising given the decrease in pH which is also observed. These antagonistic effects are not yet fully understood, but it is most likely that, the presence of the oxygen or H_2S - O_2 reaction products has an effect on the hydrogen entry efficiency

in the steel. This impact of O_2 on permeation is less pronounced in the case of the NACE A solution, containing 0.5 % acetic acid. Consequently, apart from stabilizing pH, buffers may also have an important impact on hydrogen entry, which has not yet been deeply investigated.

In order to improve the understanding of oxygen effects on corrosion mechanisms and hydrogen entry, it is proposed to carry out electrochemical impedance spectroscopy measurements on the entry face of the hydrogen permeation membrane. Some tests shall be carried at the same pH using other buffer solution to avoid acidification of test solution in presence of oxygen. It is also planned to test other H_2S/O_2 ratios by lowering H_2S content in the test medium.

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