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To cite this version:

Leandro Santos, Dayanne Menezes, Li Ke, Carol Taravel-Condat, Jean Kittel. Prediction of the flexible pipe annulus pH at high CO2 content and high temperature. Eurocorr 2017, Sep 2017, Praha, Czech Republic. hal-02462622

HAL Id: hal-02462622

https://ifp.hal.science/hal-02462622v1

Submitted on 31 Jan 2020

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Prediction of the flexible pipe annulus pH at high CO_2 content and high temperature

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Abstract

Previous works have shown that the typical ratio between the volume of electrolyte and the exposed steel surface observed in the annulus of flexible pipelines leads to a specific corrosive environment whose pH deviate from the classical thermodynamic models. In this case, due to the supersaturation in iron ions in the annulus, the commercial models even with their most recent updates cannot precisely predict the measured pH. Due to these specificities, tests are necessary to overcome these limitations and to improve with a better accuracy the pH considered in the design of the flexible pipes.

Nowadays, with the development of the Brazilian oil and gas pre-salt basins, a high CO_2 partial pressure associated with high temperature are observed in the flexible pipe annulus. Due to the lack of experimental data concerning the pH evolution under these conditions, tests were carried out with a continuous pH monitoring at CO_2 partial pressure and temperature up to, respectively, 70 bara and 84 °C.

The test results presented in this article show an amplitude between the experimental data and the predicted pH values of at least +0.4 pH units which confirms the conservatism of the thermodynamic models at saturation. In all the tests, the pH reached a maximum value after the first days of immersion followed by a decrease and fast stabilization after this event. An impact of the temperature was verified on the pH behavior in these tests.

Keywords

Flexible pipes; annulus pH; high pressure; high temperature

Introduction

Flexible pipes have been used for the transportation of crude oil, gas and water in offshore applications for more than 35 years and they are a combination of polymers and steel layers [1]. Figure 1 presents a standard representation of a flexible pipe.

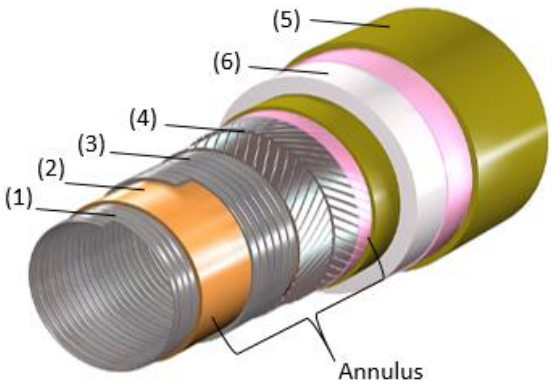

Figure 1: Layers of a typical flexible pipe.

-The first layer is a carcass (1) made of stainless steel. This layer provides resistance against the external pressure.
-The second layer (2) is a leakproof continuous polymer layer and is called the pressure sheath.
-The third layer (3) sustains internal pressure thanks to a vault wire spiraled at short pitch.
-The armours (4) are made of one or two pairs of helicoidally spiraled steel wires and are designed to ensure tensile load resistance.
-The tightness of the annulus regarding external environment is ensured thanks to an external sheath (5) made of polymer.
-If necessary, the thermal performances of the flexible pipe can be improved thanks to syntactic foam tapes (6).

Annulus environment

The annulus of a flexible pipe is defined as the space between the pressure and external polymer sheaths and it contains different gases, mainly CH_4, CO_2, H_2S and possibly water [2]. The presence of liquid water in the annulus is possible due to an accidental damage of the outer sheath that allows seawater to penetrate the annulus or due to condensation of diffused water. In that case, presence of liquid water or seawater in the annulus associated with corrosive gas such as carbon dioxide (CO_2) and hydrogen sulphide (H_2S) can lead to a corrosive and sour environment [1, 2].

Corrosion in the annulus is strongly influenced by the ratio between the free volume of electrolyte and the exposed surface of steel (V/S). Typical V/S ranges from 0.02 to 0.06 mL/cm², which corresponds to a film of electrolyte of 10 to 100 µm at the steel surface. It has been already reported that the corrosion conditions in the annular space are very specific [3,4]. In such conditions, the electrolyte pH no longer corresponds to the thermodynamic equilibrium with the acid gases partial pressures, but to a kinetic equilibrium involving iron dissolution and iron salts precipitation. The environment is highly supersaturated in ferrous ions, and the pH

exceeds by far the natural pH at saturation [4-6]. Corrosion rates are thus greatly reduced compared to the ones that would be observed in water with similar partial pressures of acid gases and without confinement.

Annulus corrosion is governed by a number of chemical, electrochemical and transport processes that occur simultaneously and that are commonly used in mechanistic models of CO_2 and H_2S corrosion [4]. When carbon steel corrodes, Fe^{2+} and an equivalent amount of alkalinity are released in the corrosion process as described in equation (1) [7].

$$Fe + 2H_2CO_3 \rightarrow Fe^{2+} + 2HCO_3^- + H_2 \qquad (1)$$

The pH in the solution increases and when the concentrations of Fe^{2+} and CO_3^{2-} ions exceed the solubility limit, the precipitation iron carbonate ($FeCO_3$) can occur [7]. When solid $FeCO_3$ is formed at the same rate as the steel corrodes, the pH becomes constant in the corroding system [7]. Nevertheless, as the precipitation of $FeCO_3$ is a slow process, Fe^{2+} and HCO_3^- can accumulate above the solubility limit, enabling a supersaturation of the annulus environment with these ions. Thus, with a low V/S, the pH of the system is higher than the pH predicted at saturation by standard thermodynamic models which fits only for very large V/S. This higher pH leads to a decrease of corrosion. It has also been reported in previous work that the higher the confinement (low V/S), the milder the corrosiveness of the annulus medium [8]. Experiments carried out at room temperature and CO_2 partial pressures (Pp) varying from 1 to 45 bara showed that the long term equilibrium pH corresponded to a high degree of super-saturation of at least + 0.5 unit above the pH at saturation. These results confirm that the flexible pipe annulus remains supersaturated even at higher CO_2 contents [5].

In the last years with the development of the Brazilian oil and gas pre-salt basins, the CO_2 partial pressure in the flexible pipe annulus has increased to an order of a few tens of bars and in most of the cases associated with high temperatures. Several experimental and modelling efforts have already been directed to predict the annulus pH, since it represents an important parameter on the material selection (carbon steel and polymer grades). Although a kinetic CO_2 model has already been proposed with a good correlation between the experimental data and the predicted supersaturated pH at high CO_2 contents at room temperature [5], there is still a lack of experimental data and understanding of the pH behaviour at confined conditions at high CO_2 content and high temperature. Thus, this paper aims at presenting the pH measurements obtained from tests under confined environment at CO_2 pressure varying from 10 to 70 bara and temperature varying from 45 to 84 °C as well as a comparison between these values and the ones predicted from thermodynamic models. An evaluation of the impact of the temperature on the pH behaviour is also given.

Experimental devices

Two test devices were used in the experiments: the first one rated to work up to 45 bara whereas the second one rated to work at pressures up to 80 bara (Figure 1). Internal pressure was continuously controlled by a pressure control valve during all the test. These test devices allow the use of gas mixtures containing N_2, CO_2 and H_2S. Carbon steel wires were used as coupons in all the testing conditions in order to achieve a volume to steel surface ratio of approximately

0.30 mL/cm^2. The solution used in the tests was composed of 35 g/L NaCl in distilled water. Table 1 presents the testing conditions.

Figure 2: Test devices for pH measurements at pressures up to 45 bara (left) and up to 80 bara (right).

Table 1: Testing conditions

Temperature (°C)	**$PpCO_2$ + PpH_2O (bara)**	**CO_2 fugacity (bara)**
45	25	22
45	70	52
84	10	9
84	70	57

Test results

The supersaturated pH (pH_{ssat}) evolution throughout the tests under the conditions described in Table 1 are presented in the graphs shown in the Figures hereafter.

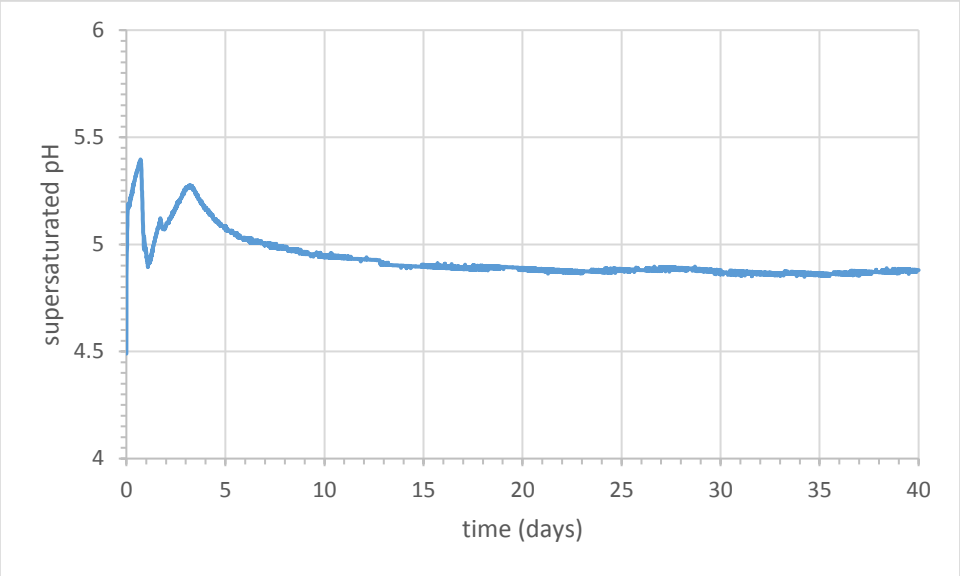

Figure 3: pH evolution under 25 bara total pressure and 45°C.

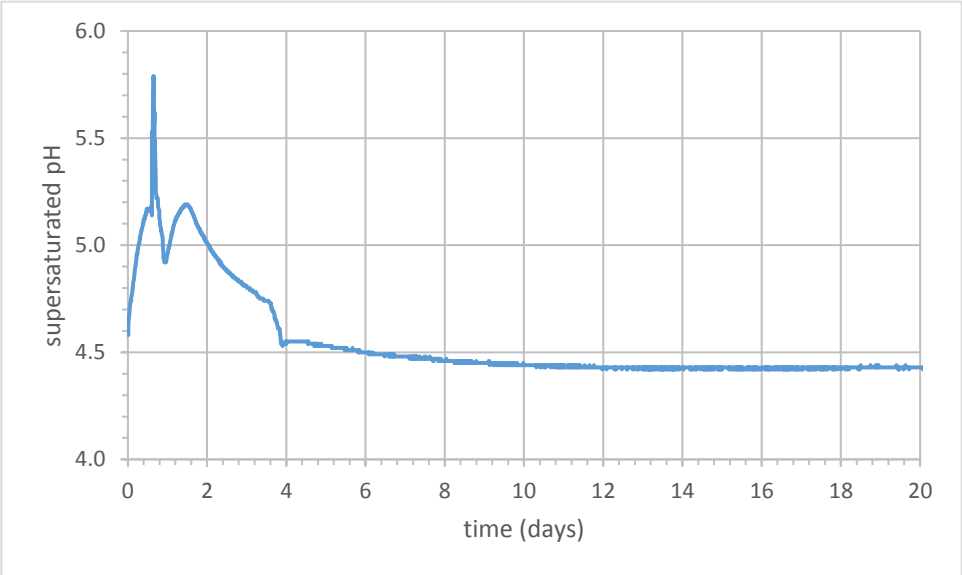

Figure 4: pH evolution under 70 bara total pressure and 45°C.

As shown in Figures 3 and 4, for the tests carried out at 45 °C it can be noted, as expected, an influence of the $PpCO_2$ on the final pH value. The higher the $PpCO_2$ the lower the pH at stabilization. A comparison between the measured supersaturated pH (pH_{ssat}) and the one predicted by the commercial software (pH_{sat}) indicates that the pH_{ssat} exceeds +0.8 the pH_{sat}

predicted for the test at 25 bara and +0.5, for the test at 70 bara. Furthermore, for both tests is noted an increase of the pH followed by a decrease and pH stabilization.

Figures 5 and 6 present the pH evolution obtained from the tests at 84 °C at, respectively, 10 bara and 70 bara total pressure.

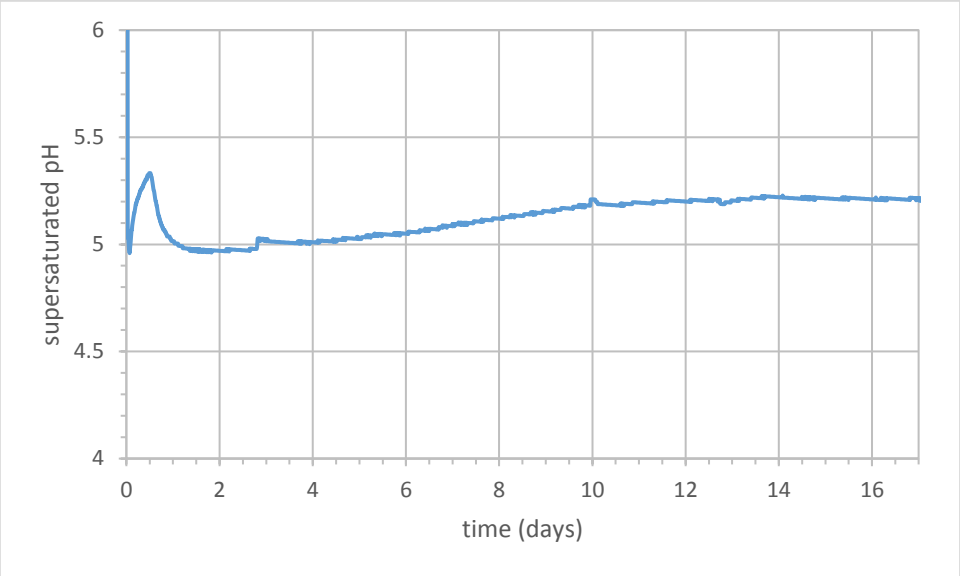

Figure 5: pH evolution under 10 bara total pressure and 84 °C.

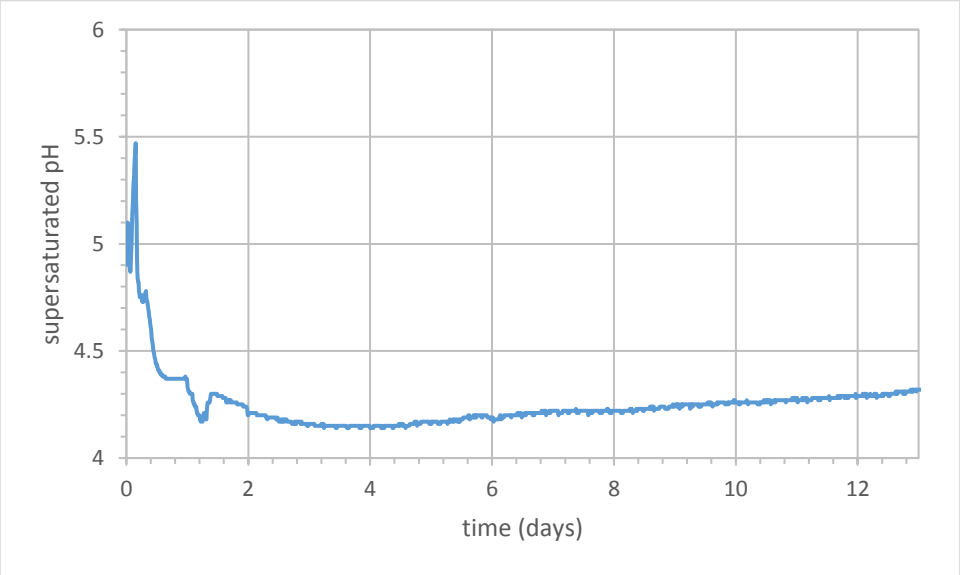

Figure 6: pH evolution under 70 bara total pressure and 84 °C.

According to Figures 5 and 6, the measured pH_{ssat} at the tests carried out at 84 °C show a similar trend as the ones observed at 45 °C. A decrease of the pH was noticed with the increase of the $PpCO_2$, as well as a fast pH increase at the beginning of the test was followed by a pH decrease and final stabilization.

For the test at 10 bara, it was considered that the stationary pH_{ssat} is 5.0, corresponding to the minimum value during the 'pseudo-plateau'. For the test at 70 bara, although pH was not completely stationary, its pseudo linear evolution with less than 0.2 pH units increase in 10 days suggested that a stable state had been obtained. In such situation, the lower pH value observed during the "plateau" was used as stable value in order to keep the highest degree of conservatism. For this test, it is thus considered that the stationary supersaturated pH is 4.1. A comparison with the pH_{sat} predicted by commercial software Cormed2™ indicates a supersaturation amplitude of +0.8 for the test at 10 bara and +0.4 for the one at 70 bara.

A summary of the measured supersaturated pH versus the predicted saturated pH is presented in Table 2.

Table 2: Summary of supersaturated pH measurements versus predicted saturated pH values.

Temperature (°C)	Total pressure (bara, $PpCO_2+PpH_2O$)	Measured supersaturated pH (pH_{ssat})	Calculated saturated pH (pH_{sat})*	Supersaturation amplitude
45	25	4.9	4.1	+0.8
	70	4.4	3.9	+0.5
84	10	5.0	4.2	+0.8
	70	4.1	3.7	+0.4

* Saturated pH was calculated with Cormed2™ with CO_2 fugacity as input, instead of CO_2 partial pressure.

The supersaturation amplitude observed in the tests is highlighted in Figure 7.

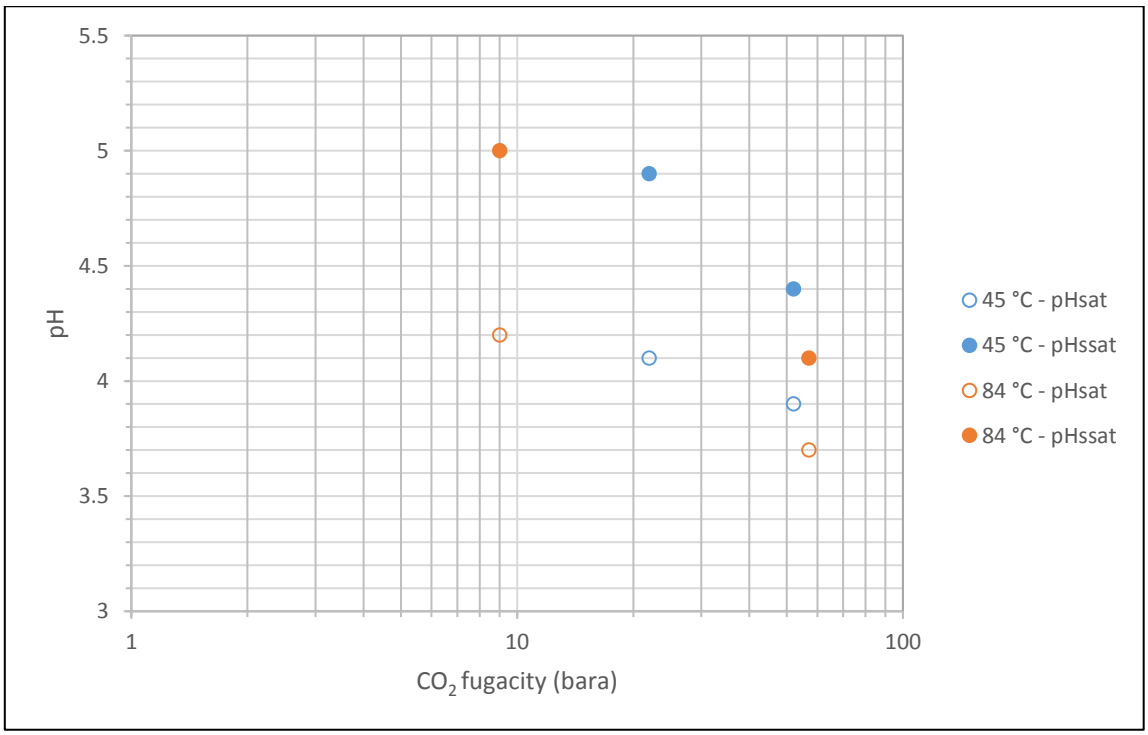

Figure 7: pH versus CO_2 fugacity (bara)

As already mentioned, it could be observed a fast increase of the pH_{ssat} reaching a maximum few hours after the beginning of the test at all the experimental conditions. After reaching this maximum, the pH_{ssat} starts to decrease and reaches the stabilization. This initial characteristic shape can be possibly attributed to the corrosion process of steel that releases Fe^{2+} ions and an equivalent amount of alkalinity in the solution as shown in equation (1) [7] as previously stated. When analyzing the impact of temperature on pH, it can be noted that for tests below 25 bara, no significant pH variation with the increase of temperature from 45 to 84 °C. In previous test carried out at 10 bara and 45 °C using the same device as the one used in these tests, the stationary pH_{ssat} was 4.9 which would confirm that the temperature has no important effect on the pH at low $PpCO_2$. On the other hand, for the tests at high pressure, it is observed the decrease of the pH_{ssat} with the temperature increase. This decrease is possibly due to the increase of $FeCO_3$ precipitation rate and, as a consequence a decrease of the ferrous ions supersaturation. Nevertheless, the supersaturation is still maintained at high CO_2 content and temperature, although with a lower amplitude than the one verified at lower pressure.

Conclusions

According to the test results it can be concluded:

- The flexible pipe annulus remains supersaturated at both high CO_2 contents and temperatures.
- For the all the range of CO_2 content and temperature, the supersaturated pH showed the same trend with a fast increase of the pH followed by its decrease and stabilization.
- No clear impact on the pH due to the temperature increase was observed up to 45 bara total pressure. For this pressure range, the pH seems to be only influenced by the CO_2 content.
- A pH decrease with the increase of temperature was noted in the tests at 70 bara total pressure. This behavior can be possibly attributed to the increase of the $FeCO_3$ precipitation rate.

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