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# Corrosive environment in the annulus of flexible pipes: pH measurements in confined conditions and under high pressure

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## Abstract

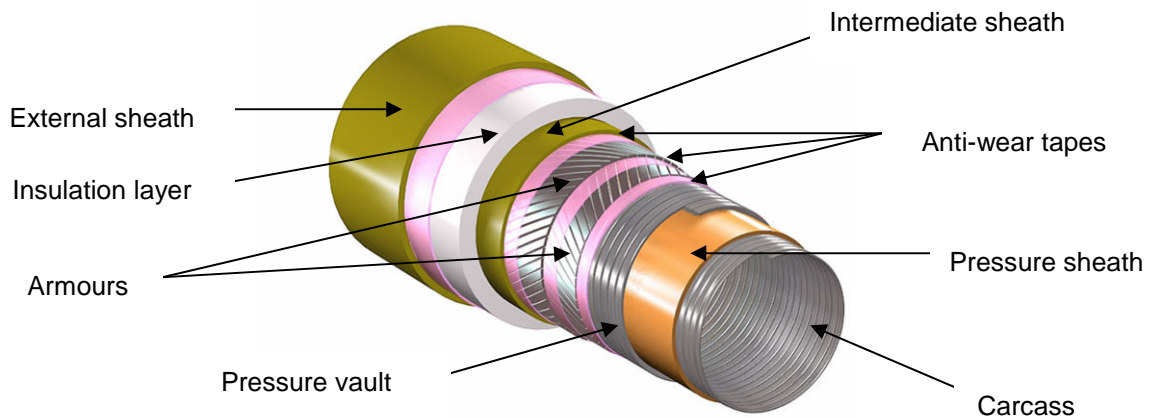
Annulus of flexible pipelines represents a specific corrosive environment for the high strength carbon steel wires, mainly due to the low V/S ratio between the volume of electrolyte and the exposed steel surface.

Corrosion experiments with continuous in situ pH measurements were performed under CO<sub>2</sub> partial pressure from 0.01 bar and up to 10 bar, and with a V/S ratio of 0.3 mL/cm<sup>2</sup>. After only a few days immersion, supersaturated pH was measured at levels close to +1 pH unit above the saturated pH calculated corresponding to iron carbonate solubility. Good correlation was found between experiments and a pH and corrosion model specially developed for confined environment. This model predicts that the corrosion rate in super-saturated conditions is considerably reduced in comparison with bulk situation.

Long term behavior was also examined. It appears that the evolution of super-saturated pH with time passes by a maximum value, then decreases slowly to a new equilibrium. It was postulated that the maximum corresponds to a fully active surface. Then, as precipitation occurs, corrosion rate is decreased by corrosion scale. The decrease of corrosion rate could be quantified from the final pH value: value as low as a few µm/year was found. Even with such low corrosion rates, high confinement still induced super-saturation effect, with final pH values at +0.5 pH units above saturated pH.

## 1 Introduction

Flexible pipelines are widely used for the transport of fluids in oil and gas applications. They are composed of successive layers of steel and polymer materials. An example of a structure of a flexible pipeline is described in Figure 1.



**Figure 1: Example of a flexible pipe structure**

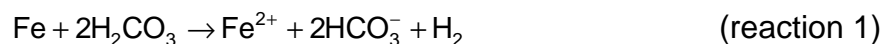
In the recent years, oil and gas production conditions evolved to higher temperature, higher pressure and greater acid gas contents, with a great incidence on materials selection. For the flexible pipelines used in offshore conditions, these conditions apply directly to materials from the bore, i.e. the carcass and the polymer pressure sheath. But there is also a great impact on the environment of the annulus, where high strength low alloy steels armor wires are used to withstand both the internal pressure and the weight of the riser. The selection and design of these steel armors needs to consider possibilities of corrosion. The presence of free water may be encountered in case of local rupture of the outer polymer sheath, allowing seawater ingress. Pure water can also be found, as a result of condensation of water vapor after permeation from the bore through the inner polymer sheath. Similarly, acid gases from the bore also permeate through the inner layer, and water with dissolved  $\text{CO}_2$  and  $\text{H}_2\text{S}$  can be found. The corrosive environment thus depends in the first place of permeation rates and equilibrium pressures of acid gases. These properties can be determined from experimental and modeling data, as described in [1]. Corrosion in the annulus is also strongly influenced by the high confinement ratio ( $V/S$ ) between the volume of electrolyte and the exposed surface of steel. Typical  $V/S$  ranges from 0.02 to 0.06 mL/cm<sup>2</sup>, i.e. corresponding to a film of electrolyte of 10 to 100  $\mu\text{m}$  at the steel surface. As already described in details, the corrosion conditions in the annular space are very specific [2-4]. 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]. 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. Lots of experimental and modeling efforts are directed to predict the annulus pH, since it represents an important parameter for materials selection for the carbon steel armors.

Until very recently, most applications presented CO<sub>2</sub> equilibrium pressure in the annulus below or close to 1 bara. However, the development of high pressure fields with up to several hundred bars of CO<sub>2</sub> moved the upper limit of CO<sub>2</sub> content in the annular space to more than a few tens of bars [5]. It became thus necessary to extend the range of available data on pH measurements in confined conditions to higher pressures. It is the goal of the present paper to show pH measurements in confined conditions at CO<sub>2</sub> partial pressures from 10 mbara to 10 bara CO<sub>2</sub>. Comparisons between experimental results and a predictive model will also be presented.

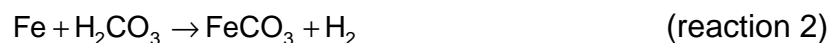
## 2 pH in confined environments

### 2.1 Modeling aspects

Leaving aside the specificities of confined environment, corrosion in the annulus of a flexible pipe can be described by chemical equilibria and electrochemical equations that are commonly used in mechanistic models of CO<sub>2</sub> and H<sub>2</sub>S corrosion [6-9]. The governing reactions are acid gases dissolutions and dissociations, reduction of proton and/or other acid components, oxidation of iron, and iron salts precipitation. In CO<sub>2</sub> environment, the global electrochemical reaction is:



This reaction produces alkalinity, thus a local increase of pH, or a global increase of bulk pH in stagnant conditions, and subsequently a decrease of corrosion rate. At the same time, HCO<sub>3</sub><sup>-</sup> is also the precipitable anion. As soon as the solubility limit is reached, iron carbonate precipitates and the whole reaction can thus be written as:



At the equilibrium and if there is no renewal of the electrolyte, the solution is then buffered by FeCO<sub>3</sub>, with a stable saturated pH (pH<sub>sat</sub>).

Now let us consider the geometrical configuration of the annulus. The main parameter is the high degree of confinement, i.e. a large surface of exposed steel with a small volume of electrolyte. Considering the worst situation, one can also make the hypothesis that there is no limitation on acid gas dissolution, nor diffusion limitations in the thin electrolyte layer.

Then, as soon as corrosion starts through reaction 1, and since it happens on a large steel surface and a small volume of electrolyte, H<sup>+</sup> ions are consumed while Fe<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup> concentrations increase extremely fast, with subsequent rise of pH and decrease of corrosion rate. For example, one can consider a system composed of pure water under 1 bar CO<sub>2</sub> at ambient temperature. Application of pH and water chemistry software shows that the initial in-situ pH is 3.9, while it reaches 5.3 at saturation in iron carbonate, corresponding to 78 ppm Fe<sup>2+</sup>. And with a confinement ratio of 1 mL/cm<sup>2</sup> and a reasonable initial corrosion rate of 0.5 mm/year, one easily

determines that saturation is reached after less than a few hours, leading to start of precipitation.

However, iron carbonate precipitation is a rather slow reaction, so that the precipitable products of the corrosion reaction  $\text{Fe}^{2+}$  and  $\text{HCO}_3^-$  are allowed to accumulate above the solubility limit, all the more so as the confinement is important. Consequently, pH increases above its saturated value (super-saturated pH,  $\text{pH}_{\text{ssat}}$ ). The corrosion subsequently decreases, until a kinetic equilibrium is reached where all corrosion products immediately precipitate.

This scheme also holds for  $\text{H}_2\text{S}$ , with a global reaction written as:



and with an intermediate electrochemical reaction producing the precipitable ions ( $\text{Fe}^{2+}$  and  $\text{HS}^-$ ) along with the buffer of the weak acid. However, the solubility of iron sulfides is much lower than that of  $\text{FeCO}_3$ , and the kinetics of the precipitation reaction is also thought to be faster so that the super-saturation effect is expected to have a lower amplitude than in the case of  $\text{CO}_2$ , provided that the corrosion rate is in the same range.

Based on these principles, a kinetic model for  $\text{CO}_2$  corrosion and pH prediction was developed, allowing to calculate the super-saturated pH and corrosion rate for various V/S and  $\text{P}_{\text{CO}_2}$  [4,10]. This model was further improved to calculate the pH transient from the start of immersion experiment until super-saturation equilibrium is reached. It is used in this paper to analyze experimental pH measurements in confined test cells.

## 2.2 Experimental verification

An experimental device was developed to allow pH measurements in confined and pressurized environment (Figure 2). In the test cell, the pH electrode is surrounded by steel coupons, with a V/S ratio of 0.3 mL/cm<sup>2</sup>. During the test, saturation of acid gases is ensured by a continuous bubbling in the solution, and gas flow rate is continuously monitored. Internal pressure is maintained by a pressure control valve, and is also monitored during all the test. A condenser placed before the pressure valve avoids liquid losses. The range of operating conditions covers 1 – 10 bara total pressure, and 4 – 80 °C. Gas mixtures containing  $\text{N}_2$ ,  $\text{CO}_2$  and  $\text{H}_2\text{S}$  can be used.



Figure 2: Experimental device for pH measurements in confined environments at pressure up to 10 bara

Experiments covering 3 decades of  $\text{CO}_2$  partial pressures were performed, from 10 mbar to 10 bara. The experimental results are compared with the pH transients calculated with the model on Figure 3.

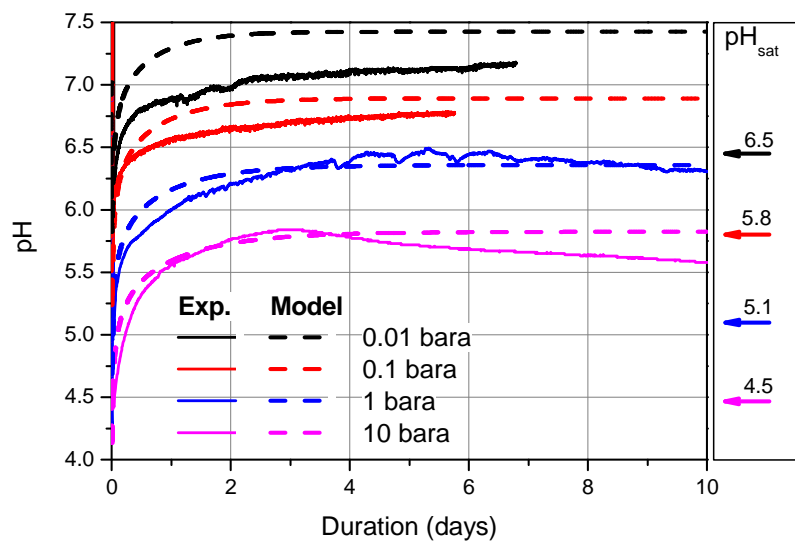
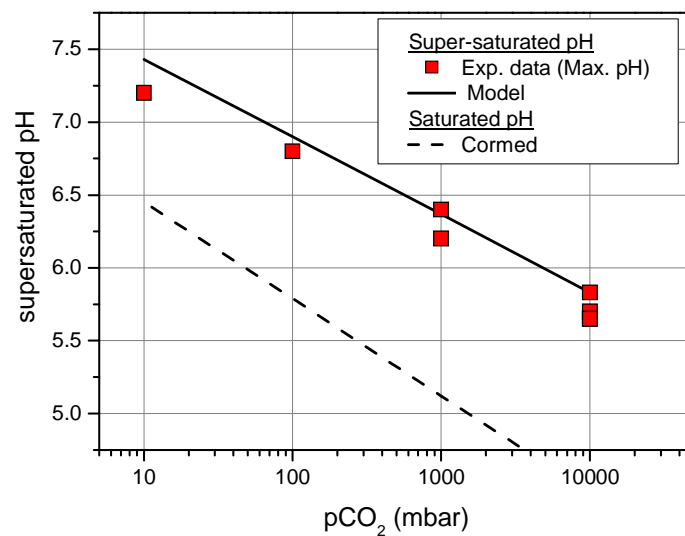


Figure 3: pH transients measured in a confined test cell ( $V/S = 0.3 \text{ mL/cm}^2$ ) with high strength steel wires exposed to 3.5 % NaCl solution at ambient temperature, and with various  $P_{\text{CO}_2}$ . Comparison with modeled data and with pH at  $\text{FeCO}_3$  saturation ( $\text{pH}_{\text{sat}}$ ).

The main trends deduced from the mechanistic analysis of § 2.1 are confirmed. pH increases sharply immediately after corrosion starts, and it takes less than a few hours to reach the pH at saturation ( $\text{pH}_{\text{sat}}$ ). A pseudo-stable super-saturation plateau

is then reached after a few days, with more than +1 pH unit difference between  $\text{pH}_{\text{ssat}}$  and  $\text{pH}_{\text{sat}}$  (Figure 4). These experimental results and the good correlation with the model confirm what had already been shown in [10]. The initial evolution of pH until this plateau is reached is well captured by the model. At this stage, the system is in kinetic equilibrium between iron dissolution occurring on a fully active surface and iron carbonate precipitation. The deviation between experimental and calculated data, which is more markedly seen at low  $P_{\text{CO}_2}$ , is probably due to an impact of water reduction in the corrosion process at this near neutral pH level which is neglected in the model.

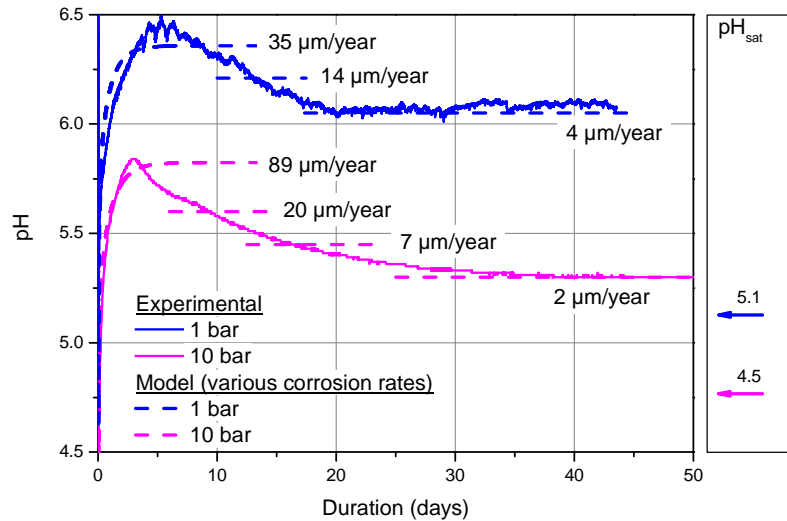


**Figure 4: Comparisons of the upper plateau of super-saturated pH with theoretical model and with saturated pH calculated with Cormed 2, for  $P_{\text{CO}_2}$  between 0.01 and 10 bara.**

The model also allows calculating the instantaneous corrosion rate during the pH transient and until the plateau is reached. In the case of 1 bara  $\text{CO}_2$ , the instantaneous corrosion rate is found to drop from more than 0.7 mm/year immediately after immersion down to 0.035 mm/year at plateau with  $\text{pH}_{\text{ssat}} = 6.5$ . Although this twentyfold decrease of corrosion rate is spectacular, the final value is still at least one order of magnitude above what is usually observed in flexible pipes. However, this theoretical corrosion rate was calculated with a confinement ratio of 0.3 mL/cm<sup>2</sup>, while the real situation is closer to 0.03 mL/cm<sup>2</sup>. At first approximation, one can consider that an increase of the confinement ratio by one order of magnitude induces an equivalent decrease of the corrosion rate. Furthermore, this plateau corrosion rate is calculated with the hypothesis that the steel surface is uniformly active, without disturbance by corrosion deposits. This is highly improbable in the annular space, where it is strictly impossible to evacuate precipitated solids. Therefore, we expect to observe a long term influence of the precipitation of corrosion products, and this is illustrated and discussed in the next paragraph.

## 2.3 Long term evolution and impact on corrosion

As seen in § 2.2, maximum super-saturated pH value is well represented by the model when one considers a fully active surface. However, long term evolution of super-saturated pH shows that the maximum value is often not stable, and that it is usually followed by a decrease of pH until a new plateau is reached. Figure 5 illustrates this trend for experiments at ambient temperature under 1 bara or 10 bara CO<sub>2</sub>. The supersaturated pH drops from 6.4 at the peak to 6.1 after three weeks under 1 bara CO<sub>2</sub>, and from 5.8 to 5.3 after six weeks with 10 bara CO<sub>2</sub>. As a first comment, it is important to note that this long term equilibrium pH<sub>ssat</sub> still corresponds to a high degree of super-saturation, since saturated pH are respectively 5.1 and 4.5 under 1 bara or 10 bara of CO<sub>2</sub>. It must also be emphasized that long term experiments are necessary to determine this equilibrium, which represents pH<sub>ssat</sub> in real service conditions with much better accuracy than too short experiments could do.



**Figure 5: Long term evolution of pH measured in a confined test cell ( $V/S = 0.3 \text{ mL/cm}^2$ ) with high strength steel wires exposed to 3.5 % NaCl solution at ambient temperature, under 1 or 10 bara CO<sub>2</sub>. Comparison with corrosion rates corresponding to various super-saturated pH's.**

This long term pH<sub>ssat</sub> evolution might be linked with an evolution of the average corrosion rate of exposed steel. As explained in the previous paragraph, the maximum supersaturated pH<sub>ssat</sub> corresponds to a fully active surface, so are the hypothesis of the modeled curves on Figure 3 and Figure 4 (100 % active surface). In practical situation, the conditions for iron carbonate precipitation are encountered extremely early. Iron carbonate super-saturation ( $SS_{\text{FeCO}_3}$ ) at the pH peak, as defined in Equation (1), was calculated by the model and gave values of 1600 at 1 bara and 4000 at 10 bara CO<sub>2</sub>.

$$SS_{\text{FeCO}_3} = \frac{\text{Fe}^{2+} \times \text{CO}_3^{2-}}{K_{\text{prec}}} \quad (\text{Equation 1})$$



In this equation,  $\text{Fe}^{2+}$  and  $\text{CO}_3^{2-}$  represent the molar concentrations and  $K_{\text{prec}}$  is the equilibrium constant of the iron carbonate precipitation reaction.

Surface scaling is therefore encountered at the very start of the experiment. It modifies the reactions at the interface. In the case of pure  $\text{CO}_2$  environment without organic acids or calcium carbonate buffer, it was shown that corrosion deposit could only induce a decrease of the corrosion rate [11]. Qualitatively, such a decrease automatically induces a decrease of pH. It is another capability of the model to calculate a reduced corrosion rate corresponding to the reduced experimental super-saturated pH, thus transforming the pH-time curve into a corrosion rate – time curve. Some results are reported on Figure 4. For example, one can calculate that the long term equilibrium pH of 6.05 under 1 bar  $\text{CO}_2$  corresponds to an average corrosion rate of 4  $\mu\text{m}/\text{year}$ . Similarly under 10 bara  $\text{CO}_2$ , long term supersaturated pH corresponds to a corrosion rate of 2  $\mu\text{m}/\text{year}$ . These corrosion rates are in excellent agreement with the feedback from long term field exposures. It is particularly remarkable that even with such low corrosion rates, the high level of confinement induces super-saturation effects, with equilibrium pH values exceeding the saturated pH by several tenths of units.

The current criteria for steel grade selection and design of flexible pipelines rely on similar long term experiments, i.e.  $\text{pH}_{\text{ssat}}$  experimentally measured. This pH evaluation method still presents a reasonable safety factor, since the real average confinement ratio in flexible pipes is ten times lower than in our experiments, which should increase the long term super-saturated pH equilibrium. For some specific areas where the local confinement is lower, it is still in the same order as in our experimental devices, which thus represents a reasonable and safe envelope for real operating conditions in the annulus.

### 3 Conclusions and perspectives

The annulus of flexible pipelines is a complex corrosive environment, which depends on acid gases and water diffusion through polymer sheaths, kinetic equilibrium between corrosion of steel surfaces, iron salts precipitation and the subsequent alkalisation of the electrolyte, and finally on interactions between corrosion products and corrosion.

In situ pH is one of the main parameters traditionally used to evaluate the potential corrosivity of oil and gas environments. pH measurements were therefore performed in specific test cells with a confinement ratio of 0.3 mL/cm<sup>2</sup> between the volume of electrolyte and the exposed steel surface. Short term experimental data obtained at  $P_{\text{CO}_2}$  between 0.01 and 10 bara showed good agreement with predictions by a kinetic model. Super-saturation amplitude close to +1 pH units was observed in comparison with saturated pH, subsequently with a decrease of the corrosion rate by at least one order of magnitude.

Long term evolution of pH in confined environment was also characterized experimentally. After a sharp increase of pH to high supersaturated values, a slow decrease was observed until a new stable equilibrium was reached. This long term

pH still remained at several tens of pH units above the saturated value. The corrosion rate corresponding to this final supersaturated pH could also be evaluated with the kinetic model, and roughly corresponded to an additional decrease of one order of magnitude, to reach corrosion rates as low as a few  $\mu\text{m}/\text{year}$ ; in excellent agreement with field data. This long term equilibrium is reached after more than three weeks in confined test cell, and it is therefore important to adopt longer exposure periods to determine relevant  $\text{pH}_{\text{ssat}}$  for real service conditions.

The main perspectives of this work concern the impact of gases mix with  $\text{CO}_2$  and  $\text{H}_2\text{S}$ . This work is already in progress. High total pressure, above 10 bara, also represents an important area of future developments.

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