Corrosion and pH prediction in the annulus of flexible pipes under high pressure of CO2

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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. This environment induces high super-saturation levels of dissolved iron, together with the establishment of pH values far above thermodynamic equilibrium. Nevertheless, it also induces difficulties to predict actual levels of pH in the annulus, since thermodynamic models do not apply.
In order to overcome these difficulties, and to obtain trustful pH values for the design of flexible pipelines, lots of efforts were put both in the experimental and modelling directions. A kinetic model was thus developed a few years ago, taking into account electrochemical and chemical reaction rates which allowed to explain super-saturated pH levels. Specific experiments consisting of continuous in situ pH measurements in confined corrosion cells confirmed the validity of the model in a pressure range 1 – 10 bar and for short term exposures.

In the present paper, the extension of experimental conditions to higher pressures of CO$_2$ is presented. A good agreement with the model prediction and the short term stabilization of in situ pH was still obtained. Furthermore, longer exposure tests were also performed. It appeared that the evolution of super-saturated pH with time went through a maximum value after a few days, but then decreased slowly to a new equilibrium. This trend was attributed to the slow build-up of an iron carbonate layer, and subsequent decrease of the corrosion rate of the metal. The first version of the kinetic model was well suited to predict the maximum pH reached after a few days, but it did not capture the slow decrease. The model was then modified, in order to take into account the impact of corrosion products precipitation on surface reactions. The new version of the model is now capable to simulate with a good accuracy the complete in-situ pH transient for durations of several weeks until stationary state is reached. It allows not only to predict stabilized super-saturated pH values, but also to quantify the steady-state corrosion rate, which usually stands below a few µm/year. 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.
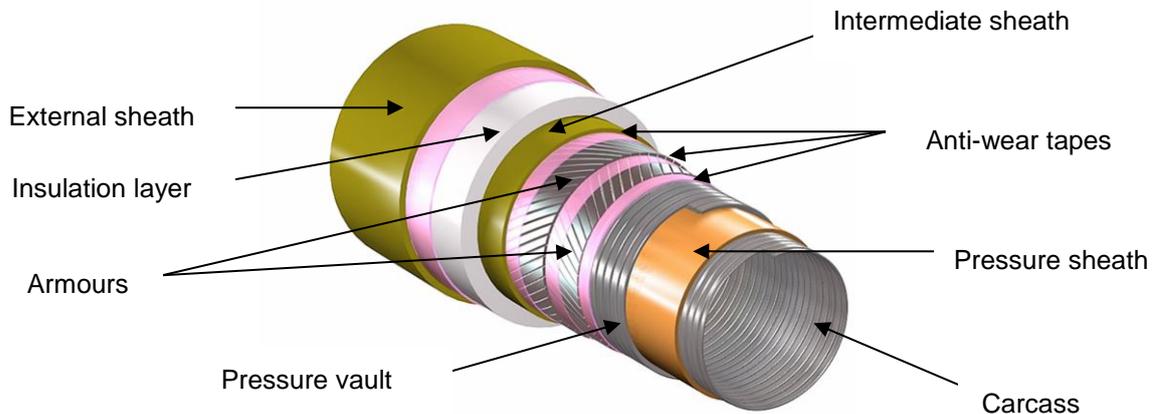

Figure 1: Example of a flexible pipe structure

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 armour wires are used to withstand both the internal pressure and the weight of the riser. The selection and design of these steel armours need to consider possibilities of corrosion. Indeed, presence of water in the annulus is possible. Seawater can be found due to accidental rupture of the outer polymer sheath, or deliberate flooding for design purposes. Pure water may also be found, as a result of condensation of water vapour 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 CO_2 and H_2S 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 modelling 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/cm², i.e. corresponding to a film of electrolyte of 10 to 100 µm 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 modelling efforts are directed to predict the annulus pH, since it represents an important parameter for materials selection for the carbon steel armours.

Until recently, most applications presented CO_2 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_2 moved the upper limit of CO_2 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.

The goal of the present paper is firstly to describe the basis of the corrosion phenomena modeling and secondly to show pH measurements in confined conditions at CO_2 partial pressures from 1 bara to 45 bara CO_2. Finally, comparisons between the experimental results and the predicted values from the model are 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_2 and H_2S 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_2 environment, the global electrochemical reaction is:

$$Fe + 2H_2CO_3 \rightarrow Fe^{2+} + 2HCO_3^- + H_2 \qquad \text{(reaction 1)}$$
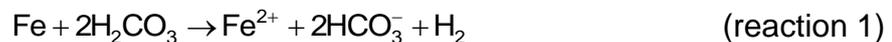
This reaction produces alkalinity, thus a local increase of pH, or a global increase of bulk pH in stagnant conditions, and subsequently a decrease of corrosion rate. At the same time, HCO_3^- is also the precipitable anion. As soon as the solubility limit is reached, iron carbonate precipitates and the whole reaction can thus be written as:

$$Fe + H_2CO_3 \rightarrow FeCO_3 + H_2 \qquad \text{(reaction 2)}$$
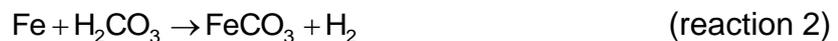
At the equilibrium and if there is no renewal of the electrolyte, the solution is then buffered by $FeCO_3$, with a stable saturated pH (pH_{sat}).

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^+ ions are consumed while Fe^{2+} and HCO_3^- 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_2 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^{2+}. And with a confinement ratio of 1 mL/cm² 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 Fe^{2+} and 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, pH_{ssat}). The corrosion subsequently decreases, until a kinetic equilibrium is reached where all new corrosion products immediately precipitate.

This scheme also holds for H_2S, with a global reaction written as:

$$Fe + H_2S \rightarrow FeS + H_2 \qquad \text{(reaction 3)}$$

and with an intermediate electrochemical reaction producing the precipitable ions (Fe^{2+} and HS^-) along with the buffer of the weak acid. However, the solubility of iron sulfides is much lower than that of $FeCO_3$, 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 CO_2, provided that the corrosion rate is in the same range.

Based upon these principles, a kinetic model for CO_2 corrosion and pH prediction was developed, allowing to calculate the super-saturated pH and corrosion rate for various V/S and P_{CO2} [4,10, 11].

Compared to the model presented in 2013 [11], improvements were made to describe the impact of precipitation on the metal surface. For instance for CO_2, the evolution with time of the total amount of precipitated $FeCO_3$ is calculated ($[FeCO_3]$), and an empirical equation is then used to calculate the corresponding residual active metal surface (Surf) (Equation 1).

$$\text{Surf (\%)} = 100 - \alpha \times [FeCO_3] \qquad \text{(Equation 1)}$$

In this equation, α is an empirical parameter, adjusted to experimental results.

As a consequence, the active surface area decreases as iron precipitates, generating a slight decrease of pH. This model is now able to fully represent experimental pH transients. It is used in this paper to analyze experimental pH measurements in confined test cells, with P_{CO2} from 1 bar to 45 bar.

2.2 Experimental verification

Experimental devices allowing to measure pH in confined and pressurized environment were used (Figure 2). In these test cells, the pH electrode is surrounded by steel coupons, with a V/S ratio of 0.3 mL/cm². 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 – 100 bara total pressure, and 4 – 100 °C. Gas mixtures containing N_2, CO_2 and H_2S can be used.

(a)

(b)

Figure 2: Experimental devices for pH measurements in confined environments at pressure up to 10 bara (a) and up to 100 bara (b)

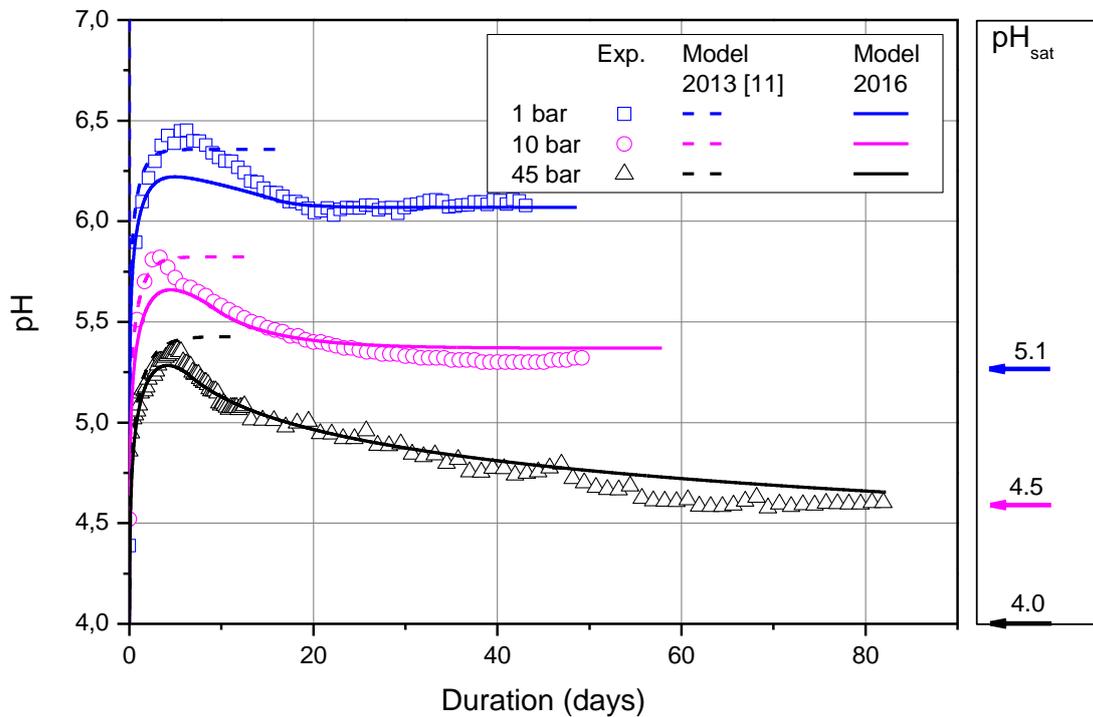The evolution of in-situ pH with time is illustrated on Figure 3 for different P_{CO2} from 1 bar to 45 bar.

Figure 3: Long term evolution of pH measured in a confined test cell (V/S = 0.3 mL/cm²) with high strength steel wires exposed to 3.5 % NaCl solution at ambient temperature, under 1 to 45 bara CO_2. Comparison with calculated pH transients with different models.

The initial rise of pH is associated with the production of alkalinity due to reaction (1). It corresponds to a parallel increase of Fe^{2+} and HCO_3^- concentrations. After a few days, pH value reaches a maximum, and starts to decrease. At this stage, the system is governed by kinetic equilibrium between iron dissolution and iron carbonate precipitation. Since the precipitation of $FeCO_3$ is a slow reaction, this kinetic equilibrium corresponds to pH values far above thermodynamic saturation of the solution with iron carbonate. For instance, in a 35 g/L NaCl solution at 1 bar CO_2, saturated pH calculated with Cormed2™ is 4.5, while the experimental value at the maximum is close to 5.8. Previous version of the model presented in 2013 [11], was already able to predict the pH transient up to this maximum value. At that time, the model could not represent the long term pH evolution. It was mentioned however that the slow long term decrease of pH was associated with the build-up of iron carbonate layer at the metal surface, resulting in a decrease of active corroding surface, hence lowering the average corrosion rate. Qualitatively, it automatically induces a decrease of pH. In order to capture this effect, the model was then modified with a function relating the evolution of active surface with the total amount of precipitated iron carbonate (Equation 1). The model was calibrated and then verified with experimental data, using a database of more than 20 long term *in situ* pH experiments up to 45 bara CO_2. In all cases, the deviation between the model and experimental results was less than 0.15 pH units.

As can be seen on Figure 3, the main experimental trends are correctly fitted, especially the long term stationary pH. It must be noted that this long term equilibrium pH_{ssat} corresponds always to a high degree of super-saturation, with + 0.5 pH units above saturated values.

In addition, the model also allows to calculate the evolution of corrosion rates with time. For the experiments of Figure 3, long term corrosion rates below 10 µm/year are predicted, 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. pH_{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. It depends on acid gases and water diffusion through polymer sheaths, kinetic equilibrium between corrosion of steel surfaces, iron salts precipitation and the subsequent alkalinisation of the electrolyte.
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/cm² between the volume of electrolyte and the exposed steel surface. Total pressure up to more than 100 bar is now experimentally accessible, with test gases containing pure CO_2 or CO_2 / H_2S mix.
In this paper, pH transients in CO_2 environments at various pressure from 1 bar to 45 bar and at ambient temperature are presented. pH increases rapidly after immersion, then goes through a maximum after a few days, and finally decreases slowly until a plateau is reached after several weeks. The final pH values still exceed saturated pH by several tenths of pH units. This long term equilibrium is reached after more than three weeks in confined test cell, and therefore longer exposure periods must be adopted to determine relevant pH_{ssat} for real service conditions. At room temperature, a minimum test duration of two months is often needed.

A predictive model, derived from the 2013 version, is now able to represent surface evolution associated with iron carbonate precipitation. pH evolution with time can be calculated. A good fit with experimental data is obtained for conditions up to 45 bara of CO_2. The model also predicts final corrosion rates below 10 µm/year for the tests between 1 and 45 bar CO_2 and a confinement of 0.3 mL/cm².

Further work is ongoing to take into account the effects of H_2S and temperature into the model.

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