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# A KINETIC MODEL OF CO₂ CORROSION IN THE CONFINED ENVIRONMENT OF FLEXIBLE PIPE ANNULUS

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## ABSTRACT

Flexible pipes used in the offshore industry are composed of steel wires enclosed in an annulus formed by inner and outer thermoplastic sheaths. The $CO_2$ corrosion of the carbon steel wires located in the annular space occurs within restricted volumes of electrolyte. For instance, the typical V/S ratio between the volume of electrolyte and the exposed steel surface is in the order of 0.03 mL.cm$^{-2}$. In such confined environments, corrosion measurements clearly show that the results classically obtained in bulk conditions (infinite electrolyte volume) do not remain valid.

From a theoretical point of view, the effect of confinement is usually ignored by available $CO_2$ corrosion models, so that experimental results strongly deviate from predictions when the V/S ratio decreases. Thus, the corrosion rates measured in the annulus conditions are commonly 2 or 3 orders of magnitude lower than those predicted and the measured pH are significantly higher than the saturation pH predicted by thermodynamic models such as CORMED.

In this context, a new kinetic model of the physico-chemical processes occurring during the corrosion of steel covered by a thin liquid film and exposed to a pure $CO_2$ atmosphere was developed. From a qualitative point of view, this model allows to explain theoretically some unusual physico-chemical phenomena classically observed in such corrosive and confined environments: iron supersaturation, high values of pH, low corrosion rates, and their dependence with the V/S ratio. The paper also presents the results of tests and measurements performed in the annulus of flexible pipes and shows that the model agrees well with the measurements.

Keywords: $CO_2$ corrosion, modelling, super-saturation, siderite, flexible pipelines

## I. INTRODUCTION

Used for 30 years in offshore applications, flexible pipelines are more and more widespread elements for the transport of crude oils on the sea bottom (flowlines) and then to the topside equipments (risers). Easy to install, these pipes are notably well adapted to deep water production. The main elements which constitute the structure of flexible pipes are depicted in Fig.1.
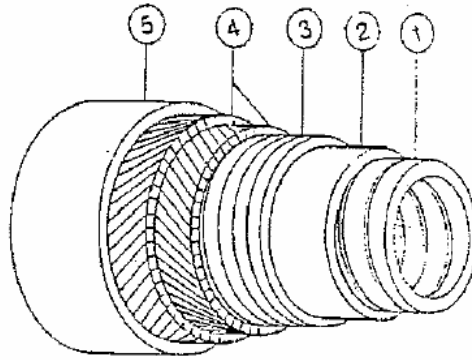


*Figure 1: Flexible pipeline cross section*

With:

1. An interlocked internal carcass usually made of stainless steel. Its purpose is mainly to prevent collapse of the inner sheath due to the high hydrostatic pressure. This carcass is not leak-tight against gas and liquid.
2. An inner polymer sheath which seals the bore. Depending on the field temperature conditions, this polymer layer is made of P.E., polyamide 11 or PVDF.
3. One or two layers of pressure armours.
4. Two or four layers of cross wound wires to give the pipe axial strength (tensile armours).
5. An outer plastic sheath for sealing and protection of the inner metallic components.

The annulus is defined as the space located between the two polymer sheaths (marked 2 and 5 on Fig. 1).

During the pipe service, the annulus may be filled with an electrolyte which can be condensed water (as a result of water permeation through the inner sheath) or sometimes sea water (in case of accidental tearing of the outer sheath). Acid gases contained in the crude oil ($CO_2/H_2S$) also permeate into the annulus through the inner sheath. In these conditions, the armouring wires located in the annulus could corrode uniformly. As a corrosive environment, the annulus is however quite specific because of the high level of confinement of the electrolyte. Indeed, the ratio V/S between the volume of electrolyte and the exposed metallic surface is typically ranging between 0.02 and 0.06 $mL.cm^{-2}$ inside the annulus. In the case of a pure $CO_2$ environment, the annulus can be depicted schematically by Fig. 2.
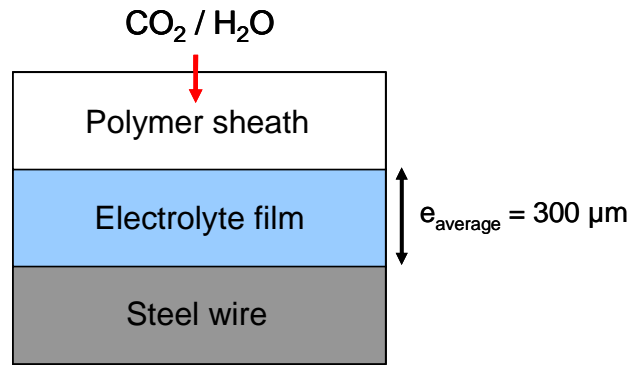
*Figure 2: Schematic description of the annulus in the case of a pure $CO_2$ environment*

In the situation of confinement encountered in the annulus (see Fig. 2), it is now well admitted that the corrosion behaviour of steel differs drastically from the one observed in bulk conditions (infinite electrolyte volume) at the same temperature and for the same pressure of acid gas [1-4]. Past studies [1] revealed notably that both corrosion rates and pH depend on the thickness of the electrolyte layer covering the steel surface. Hence, it was shown that, as the V/S ratio decreases, corrosion rates systematically decrease while during the same time the measured pH increases [2,3].

Thus, the $CO_2$ corrosion rates of steel are radically inhibited by the geometrical confinement of the electrolyte in the annulus conditions [1-4]. At 20°C, Ropital *et al.* [1] evidenced, as an example, that $CO_2$ corrosion rates of low alloyed steel immersed in an electrolyte saturated with $CO_2$ ($P_{CO2}$ = 1 bar) could be reduced by a factor 400 when the V/S ratio diminishes from 100 to 0.25 mL.cm$^{-2}$. More generally, laboratory measurements [1,2,4] show that the corrosion rates in confined environments such as the annulus are commonly 2 or 3 orders of magnitude lower than those predicted by the classical $CO_2$ corrosion models [5-9]. Results from full scale experiments performed by Technip [3] and the durability of the flexible pipelines currently in service all over the world provide some additional strong evidences of the weakness of the corrosion rates in the annulus of offshore flexible pipelines.

Available studies [1-4] also report that the very low corrosion rates observed in the annulus are coupled with high values of pH. Hence, the measured pH can sometimes exceed by 1 unit the saturation pH calculated from thermo-dynamical models as CORMED which fit experiments only for very large V/S ratios [1,2,10,11]. For instance, under 1 bar of $CO_2$ at 20°C, the pH measured for V/S lower than 1,4 mL.cm$^2$ are above 6 while the saturation pH predicted by CORMED is equal to 5.3 [1,2]. Furthermore, as already mentioned previously, in such confined corrosive environments, it was also shown that the pH increases as the V/S ratio decreases [1,2].

The high values of pH observed in the annulus are generally explained qualitatively by the Fe(II) super-saturation of the solution confined in this space [1-4,12-14]. The occurrence of this super-saturation state and the empirical dependence between pH and V/S ratio are totally unpredicted by thermodynamics [10,11]. These two important points clearly underline that the use of a simple thermo-dynamical description is not well adapted to the case of confined environments such as the annulus.

In fact, the models cited previously [5-11] were developed on the basis of bulk hypothesis (infinite electrolyte volume) and do not take into consideration the specificities of the mass transport in confined aqueous environments (accumulation of corrosion products, low concentration gradients). This inadequacy between the situations described (confinement) and

the hypotheses retained (bulk) can explain the discrepancy between model predictions [5-11] and measurements at low V/S.

Recently, some attempts were made to develop models more suitable to describe the corrosion processes occurring under thin electrolyte films [15-17]. However, these models focused specifically on corrosion rate prediction [15] with no indication concerning pH. Thus, the particular physico-chemical behaviour (the Fe(II) super-saturations, the low corrosion rates, the high pH values and their respective dependence on the V/S ratio) observed in confined aqueous environments such as the annulus still remains poorly understood.

Thus, up to now, due to this lack of adapted models, some of the physico-chemical parameters (corrosion rates and pH) required for the design of flexible pipelines are still calculated using very conservative models which do not take into account the specificity of the confinement existing in the annulus. For instance, the saturation pH predicted by CORMED [10,11] is generally used as the reference pH in the annulus whereas, as discussed previously, all available experiments [1-4] show that real pH are higher than this theoretical thermodynamic pH. As a summary, currently, the use of such pessimistic models leads to a clear overestimation of the severity (corrosion rates, pH) of the annulus environment.

In this context, the aim of the present paper is to propose a more realistic modelling of the physico-chemical processes occurring during the $CO_2$ corrosion of the armour steel wires located in the annulus of offshore flexible pipelines. This model, based on a kinetic approach quite similar to the one used in the case of top of line corrosion by Nesic's group [17-20], is presented in section II of the present paper. In section III, results obtained from the models will be discussed with respect to available experimental data. The pH calculated from the model will be compared in particular to the saturation pH predicted by the thermodynamic model CORMED.

## II. DERIVATION OF THE MODEL

The simplified geometry of the annulus considered in the model is described in Fig. 2. In the present version of the model, $CO_2$ is the only acid gas supposed to be present in the annulus.

The seven physico-chemical processes taken into account and reported in Table 1 are the following: the two heterogeneous electrochemical reactions occurring during the corrosion of steel ((I) and (II)), the homogeneous dissociations of dissolved $CO_2$ ((V) and (VI)) and water (VII), the heterogeneous siderite precipitation (III), and the heterogeneous dissolution of $CO_2$ (IV). The water dissociation reaction is assumed to be fast enough to be at thermodynamic equilibrium ($K_e = 10^{-20}$ mol$^2$.cm$^{-6}$). Such equilibrium hypothesis is not made for the other processes considered.

Due to the possible precipitation of siderite ($FeCO_3$) [1,17-20] and due to the eventual presence of grease on the armour steel wires, the steel surface could be partially blocked by an insulating film in the annulus. Then, a parameter $\theta$ (dimensionless) corresponding to the coverage ratio of the surface by such insulating films will be used in the present paper.

Under thin electrolyte layer conditions (as encountered in the annulus of offshore flexible pipelines), experience shows that uniform corrosion rates are low [1-4]. In such context, it is assumed that the rates of interfacial processes are not limited by mass transport. Then, the concentrations of dissolved species will be supposed homogeneous in the liquid film and heterogeneous reaction rates (processes I, II, IV) will be converted into homogenous production rates (see Table 1) according to relation (1):

4

$$N_i = j_i \cdot (S/V) \tag{1}$$

With $N_i$ homogeneous production rate of the heterogeneous reaction i (mol.s$^{-1}$.cm$^{-3}$)
  $j_i$ rate of the heterogeneous reaction i (mol.s$^{-1}$.cm$^{-2}$)
  S/V ratio between the exposed metallic surface and the liquid volume (cm$^{-1}$)

| Reaction | Reaction equation | Homogeneous production rate (mol.cm$^{-3}$.s$^{-1}$) | Ref. |
|---|---|---|---|
| Anodic dissolution (I) | $Fe \rightarrow Fe^{2+} + 2\ e^-$ | $N_a = \dfrac{S}{V} \cdot \dfrac{1}{2.F} \cdot (1-\theta) \cdot i_{0_a} \cdot 10^{\frac{E-Erev}{b_a}}$ | [18] |
| Cathodic reaction (II) | $2\ H^+ + 2\ e^- \rightarrow H_2$ | $N_c = \dfrac{S}{V} \cdot \dfrac{1}{F} \cdot (1-\theta) \cdot i_{0_c} \cdot c_{H^+}^{0.5} \cdot 10^{-\frac{E-0.06 \cdot pH}{b_c}}$ | [18] [21] |
| Siderite precipitation (III) | $Fe^{2+} + CO_3^- \Leftrightarrow FeCO_3$ | $N_{prec} = k_1 \cdot c_{Fe^{2+}} \cdot c_{CO_3^{2-}} - k_{-1}$ | [14] |
| Gas dissolution (IV) | $CO_{2(g)} \Leftrightarrow CO_{2(aq)}$ | $N_{diss} = \dfrac{S}{V} \cdot \left( k_2 \cdot P_{CO2} - k_{-2} \cdot c_{CO_{2(aq)}} \right)$ | [22] [23] |
| First acid dissociation (V) | $CO_{2(aq)} \Leftrightarrow HCO_3^{2-} + H^+$ | $N_{ac_1} = k_3 \cdot c_{CO_{2(aq)}} - k_{-3} \cdot c_{H^+} \cdot c_{HCO_3^-}$ | [24] |
| Second acid dissociation (VI) | $HCO_3^- \Leftrightarrow CO_3^{2-} + H^+$ | $N_{ac_2} = k_4 \cdot c_{HCO_3^-} - k_{-4} \cdot c_{H^+} \cdot c_{CO_3^{2-}}$ | [24] |
| Water dissociation (VII) | $H_2O \Leftrightarrow OH^- + H^+$ | $K_e = c_{OH^-} \cdot c_{H^+}$ | [10] |

Table 1: Physico-chemical processes considered and corresponding production rates

The steady state is supposed to be achieved. Under this assumption, the concentrations of dissolved species do not depend on time so that the following relations (2) are verified:

$$\frac{\partial c_{Fe^{2+}}}{\partial t} = \frac{\partial c_{H^+}}{\partial t} = \frac{\partial c_{CO_{2(aq)}}}{\partial t} = \frac{\partial c_{HCO_3^-}}{\partial t} = \frac{\partial c_{CO_3^{2-}}}{\partial t} = 0 \tag{2}$$

Using (1) and the homogeneous production rates as defined in Table 1, relations (2) can be written more explicitly:

$$\frac{S}{V} \cdot \frac{i_{corr}}{2 \cdot F} = N_a = \frac{1}{2} \cdot N_c = N_{prec} = N_{diss} = N_{ac_1} = N_{ac_2} \tag{3}$$

with   $i_{corr}$ the corrosion current density (A.cm$^{-2}$)
    F the Faraday constant (96500 C mol$^{-1}$)
    $N_i$ the homogeneous production rate of reaction i (mol.s$^{-1}$.cm$^{-3}$ ; see table 1)

Otherwise, the charge balance in the solution and the water dissociation equilibrium are expressed as:

$$2 \cdot c_{Fe^{2+}} + c_{H^+} = c_{HCO_3^-} + c_{OH^-} + 2 \cdot c_{CO_3^{2-}} \tag{4}$$

$$K_e = c_{OH^-} \cdot c_{H^+} \qquad (5)$$

Finally, from the set of eight equations constituted by (3), (4), and (5), the six unknown concentrations, the corrosion rate $i_{corr}$, and the corrosion potential $E_{corr}$ (i.e. rest potential of the steel where $i_{corr} = i_a = i_c$) could be easily calculated in the annulus as a function of V/S, $P_{CO2}$ and $\theta$ at the steady state.

## III. RESULTS AND DISCUSSION

The constants used for the calculations reported in Figs. 3 to 7 of this paper were taken from the literature at 20°C [7,10,11,14,18,22-27]. Calculated concentrations (pH and $Fe^{2+}$) were compared to the values returned in the same conditions by the commercial model CORMED (version 2) which assumes that thermodynamic equilibrium is achieved within the liquid phase [10,11]. This latter assumption is in fact equivalent to consider an infinite electrolyte volume.

In order to quantify more clearly the degree of super-saturation of the solution with respect to $Fe^{2+}$ concentration [11-13], Fe(II) concentration will be discussed in the present article in terms of super-saturation factor ($SF_{Fe}$) as defined by relation (6).

$$SF_{Fe} = \frac{c_{Fe^{2+}}}{[c_{Fe^{2+}}]_{eq}} \qquad (6)$$

where $[c_{Fe^{2+}}]_{eq}$ is the concentration of Fe(II) at the thermodynamic equilibrium

The influence of the V/S ratio was first investigated for different $\theta$ values. A particular attention was paid to the limiting case $\theta = 0$, corresponding to a totally active steel surface, and $\theta = 1$, corresponding to a totally blocked surface (*i.e.* no interfacial flux which implies the achievement of the thermodynamic equilibrium). Results obtained with a $CO_2$ partial pressure of 1 bar are presented in Figs. 3 to 5.
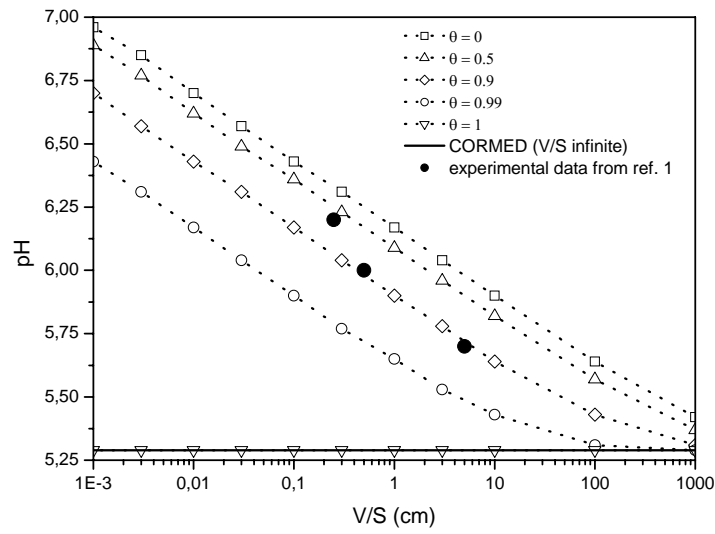
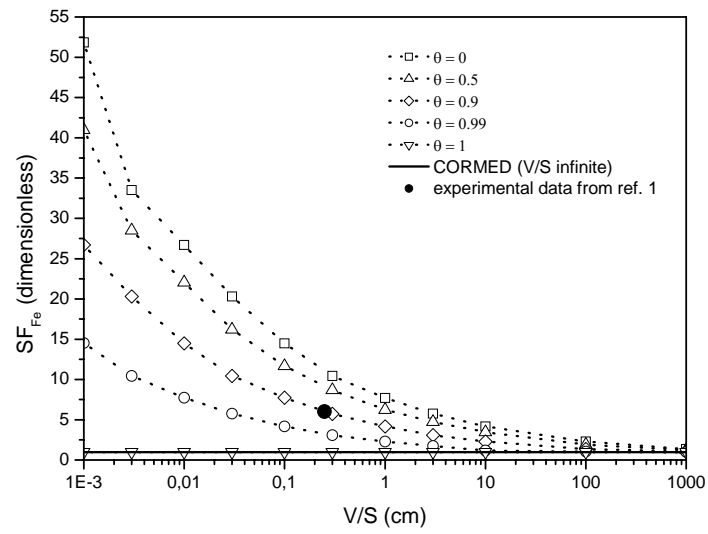*Figure 3 : Evolution of the pH with the V/S ratio for different θ ; $P_{CO2}$ = 1 bar*



*Figure 4 : Evolution of the Fe II sursaturation factor $SF_{Fe}$ with the V/S ratio for different θ ; $P_{CO2}$ = 1 bar*
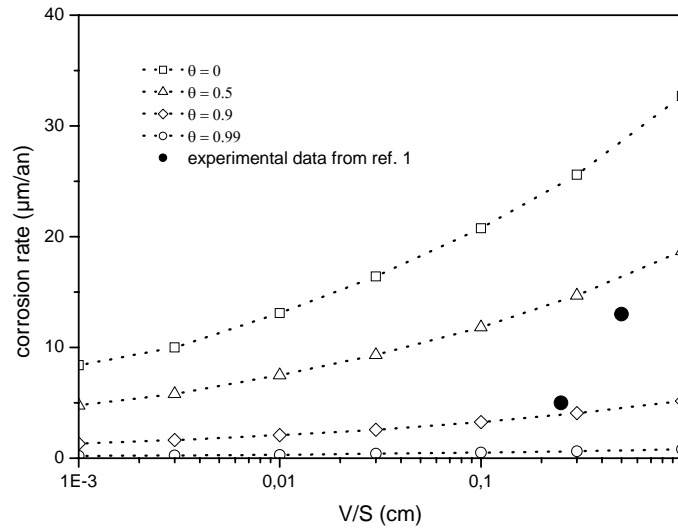
*Figure 5* : *Evolution of the corrosion rate with the V/S ratio for different θ ; $P_{CO2}$ = 1 bar*

In agreement with experience, the pH value, the Fe(II) concentration, and the corrosion rates calculated from the model vary with the V/S ratio (Figs. 3 to 5). Hence, for $P_{CO_2}$ = 1 bar, the pH increases from 5.29 in bulk conditions to values higher than 6 for V/S ratios inferior to 0.01 cm (Fig. 3). In the same trend, as the V/S ratio decreases, $SF_{Fe}$ increases to reach values of the order of 10 for V/S ratios inferior to 0.01 cm (Fig. 4). Concerning corrosion rates, they decrease when V/S ratios decrease. In the case of V/S ratios inferior to 1 cm, the order of magnitude of the predicted corrosion rates is 10 µm/year for 1 bar of $CO_2$ (Fig. 5).

The dependence on the V/S ratio, experimentally observed [1-4], has never been clearly evidenced by other existing models [15-17] and remains totally unpredicted by thermodynamics. For high V/S ratios, $SF_{Fe}$ and pH tend towards thermodynamic values (Figs. 3 and 4), showing that the kinetic model proposed is consistent with the CORMED model (hypothesis adapted for bulk conditions).

In agreement with Ropital's experiments [1], for small V/S ratios, the corrosion rates (Fig. 5) remain much lower than those predicted by the bulk corrosion models under the same $CO_2$ partial pressure (from 0.85 to 3.7 mm/year according to [6] and [9]). Moreover, the effect of θ on the corrosion rates is significant in Figs. 5 and 7. As already suggested by Vitse *et al.* [17], the comparison between the model predictions and the experimental results [1] shows that the blocking nature of the siderite deposit (θ ≠ 0) should be taken into account to avoid an overestimation of the corrosion rates at low V/S.

Calculated pH values are weakly sensitive to the value of θ. Indeed, changing θ from 0 to 0.9 induced a maximum pH change of 0.3 units, in the whole ranges of V/S and $P_{CO2}$ investigated (see Figs. 3, 6 and 8). As a totally blocked surface (*i.e.* θ → 1 and $i_{corr}$ → 0) is reached, the pH values tends towards thermodynamic pH values (see Figs. 3 and 6). This is consistent with the definition of a thermodynamic equilibrium state (steady state with all current densities equal to zero). It is however interesting to note that even a very little activity of the steel surface has a large impact on the calculated pH values. Hence, for instance, in the case of a steel surface blocked at 99% (by grease or siderite), under 1 bar of $CO_2$, the pH still exceed saturation pH from nearly 0.7 unity for a V/S ratio equal to 0.03 cm (see Fig. 3).

In the case of a V/S ratio of 0.03 cm (average value in the annulus of flexible pipelines), the impact of the $CO_2$ partial pressure on pH and corrosion rates is depicted respectively in Figs. 6 and 7. As expected, when $CO_2$ partial pressure increases, pH decreases while the corrosion rates increase. Nevertheless, the calculated pH values always remain above the saturation pH predicted by thermodynamics. Accordingly, the corrosion rates stand at levels much lower than those expected in bulk conditions [6,9].
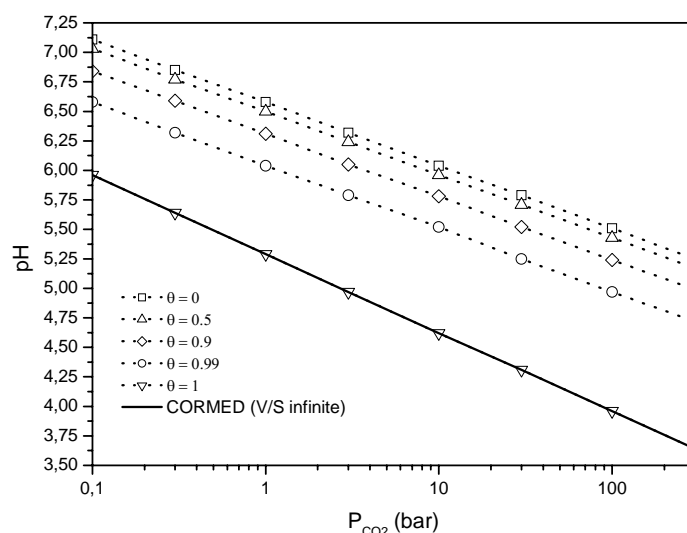


*Figure 6 : Evolution of the pH with the $CO_2$ partial pressure for different θ ; V/S = 0.03 cm*
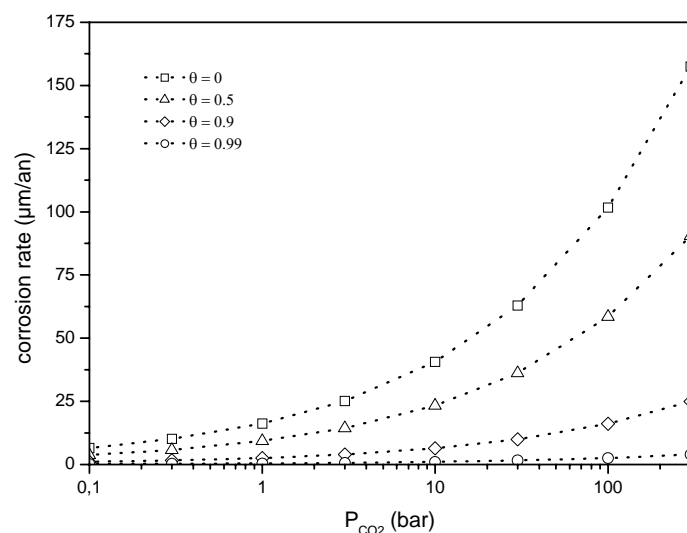


*Figure 7 : Evolution of the corrosion rate with the $CO_2$ partial pressure for different θ ; V/S = 0.03 cm*

In Fig. 8, experimental pH data collected from different studies performed by Technip and IFP are compared to the pH predicted by the model.
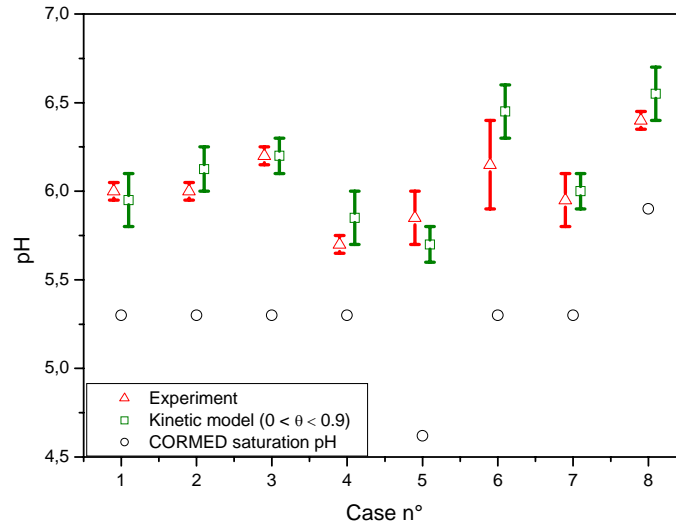
*Figure 8 : Comparison between experimental pH, pH calculated from our new model and saturation pH calculated from CORMED for different cases taken from the litterature ($P_{CO_2}$ ranged between 0.1 and 10 bar, V/S between 0.03 and 5 mL.cm$^{-2}$, 20°C).*

The pH calculated from the model fit well with the experimental pH measured. In confined environments containing pure $CO_2$ such as the annulus, Fig. 8 illustrates the improvement of the pH predictions provided by the kinetic model proposed in this article in comparison with the pH prediction made using the CORMED saturation pH.

Finally, the kinetic approach used in the model systematically led to the calculation of Fe(II) concentrations and pH values higher than those predicted by thermodynamics (see Figs. 3,4,6, and 8). This situation, in agreement with field observations, is a direct consequence of the slow kinetic of the siderite precipitation reaction. Moreover, due to the relatively high pH values observed in the confined environment, the calculated corrosion rates always remain relatively low even for a totally active steel surface ($\theta = 0$). The comparison between the model and the experiments indicate however that the values of $\theta$ are higher than 0.5 at 20°C in confined environments containing dissolved $CO_2$.

## IV. CONCLUSION

A kinetic model of the physico-chemical processes occurring during the corrosion of the armour steel wires located in the annulus of offshore flexible pipelines was proposed in the case where the thin water film covering the steel surface is exposed to a pure $CO_2$ atmosphere. This model explains theoretically the links between pH, corrosion rates, V/S ratio, the blocking ratio of the steel surface, and $CO_2$ partial pressure. The Fe(II) super-saturation, the low corrosion rates, and the high values of pH usually observed in the annulus conditions (low V/S ratio) are well predicted by the model. The model underlines the weaknesses of the thermodynamic approach when it is used to calculate pH in confined environments such as the annulus. In the case of pure $CO_2$ environment, the model particularly points out the pessimistic character of the pH predictions made using the saturation pH calculated from CORMED.

For practical purposes, the model will provide improved quantitative estimation of the pH values, the corrosion rates, and the Fe(II) concentrations in the annulus space of flexible pipelines. Currently, work is in progress to adapt the model to the case of sour corrosion by taking into account the existence of an $H_2S$ partial pressure in the gas phase. The influence of the temperature will also be taken into account in the next version of the model.

In sour service applications, the optimization of the pH prediction in the annulus would permit in certain cases the use of higher mechanical strength wires.

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