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Corrosion mechanisms in aqueous solutions containing dissolved H₂S. Part 2: Model of the cathodic reactions on a 316L stainless steel rotating disc electrode

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Abstract: In H₂S containing solutions, the reduction of protons with a buffer effect contributing to the transport of protons at the steel surface, is not sufficient to explain the cathodic polarization curves obtained on 316L stainless steel. An additional electrochemical reaction was observed and was attributed to a direct H₂S reduction. A numerical model is presented with these hypotheses and a good agreement is found with the experimental data presented in a previous paper. With this model it is also possible to present the concentration profiles of the different species involved in the cathodic process.

Constant	Value	References
ν	$0.01 \text{ cm}^2 \text{ s}^{-1}$	
D_{H^+}	$9.3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$	[6]
D_{H_2S}	$1.6 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$	[6]
D_{HS^-}	$2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$	[6]
k_{H^+}	$3 \times 10^{-11} \text{ mol}^{0.5} \text{ cm}^{-0.5} \text{ s}^{-1}$	[1]
k_{H_2S}	$6 \times 10^{-12} \text{ mol}^{0.5} \text{ cm}^{-0.5} \text{ s}^{-1}$	This study
b_{c,H^+}	120 mV	[6]
b_{c,H_2S}	145 mV	[1]
k_1	0.2 s^{-1}	This study
$K_1 = \frac{k_1}{k_{-1}}$	$10^{-10} \text{ mol cm}^{-3}$	[7]
K_2	$10^{-22} \text{ à } 10^{-15}$	[7]

Table 1

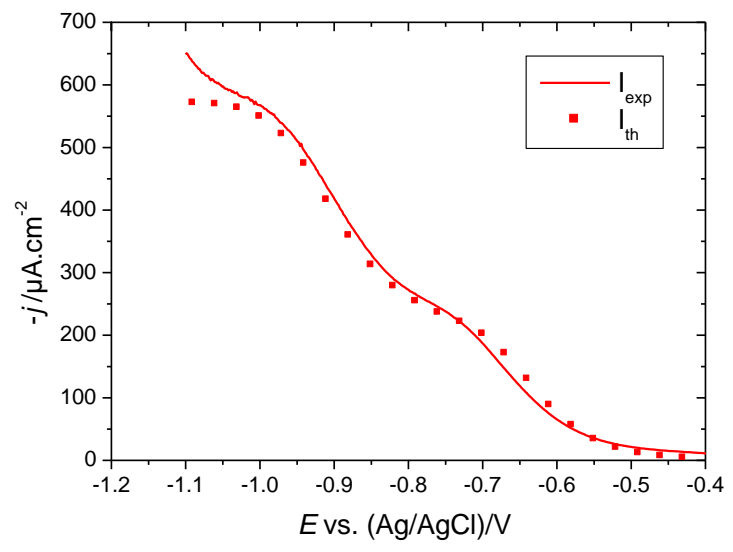


Figure 1

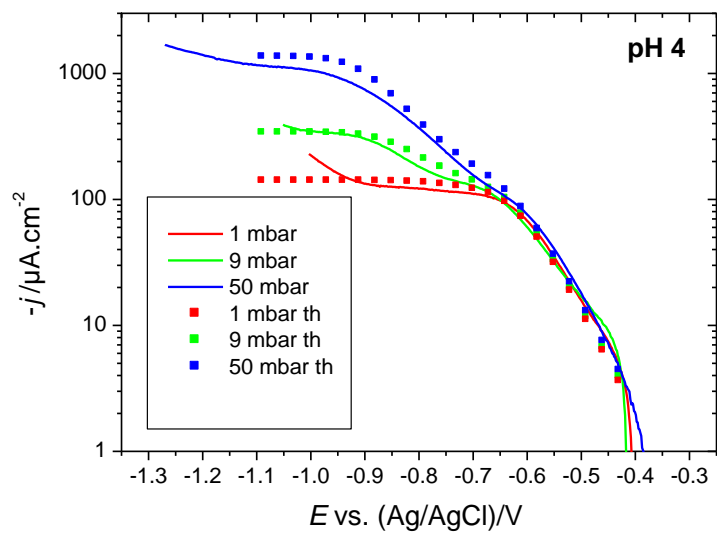


Figure 2

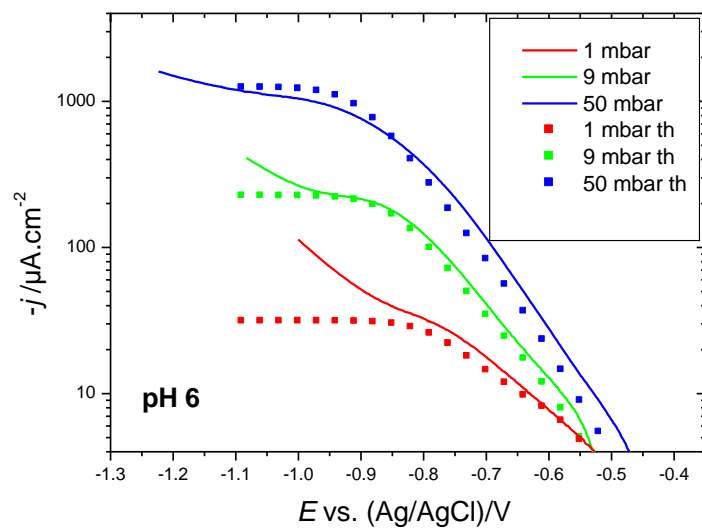


Figure 3

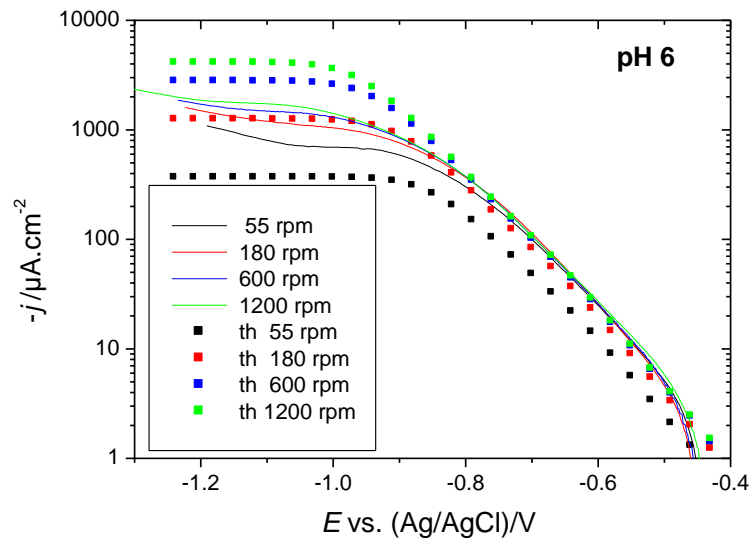


Figure 4

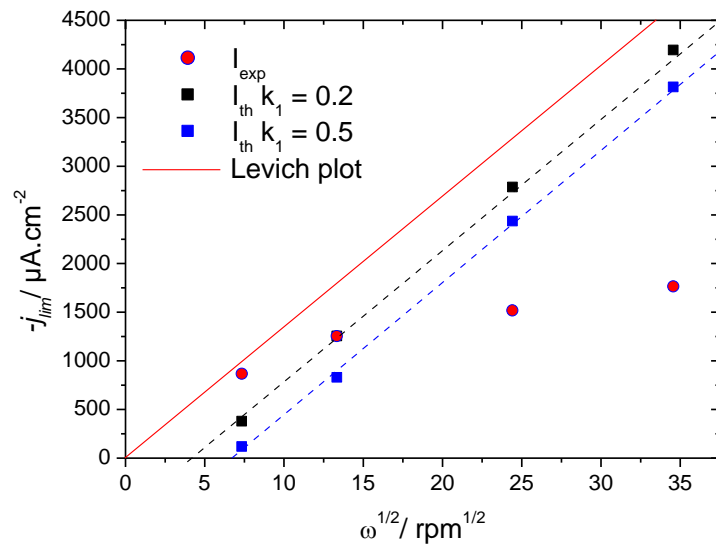


Figure 5

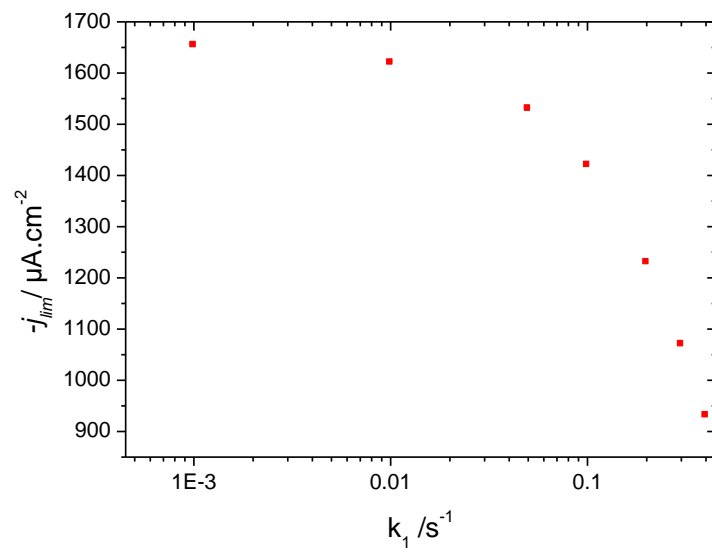


Figure 6

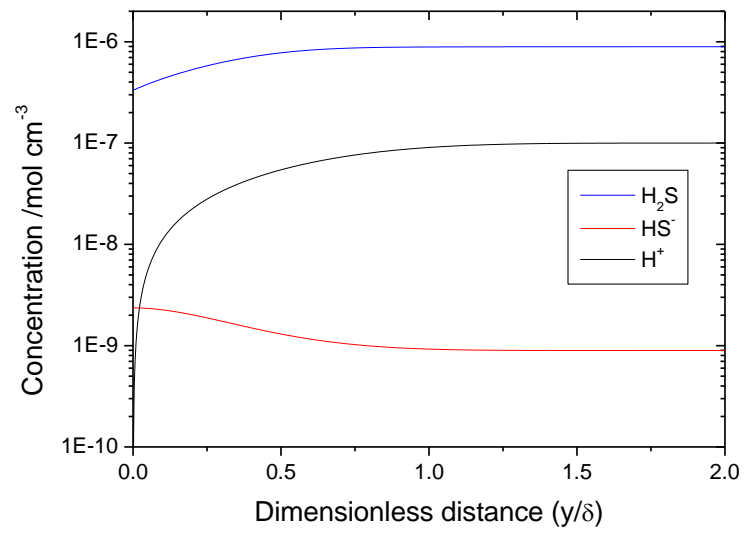


Figure 7

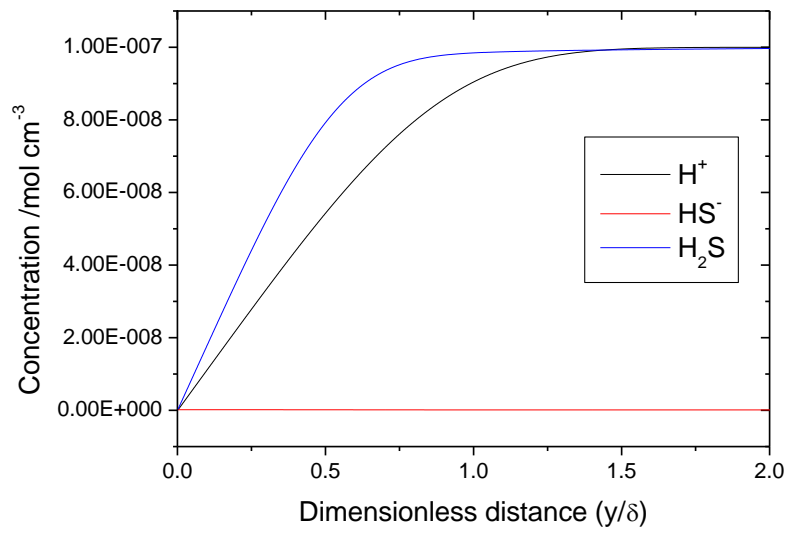


Figure 8

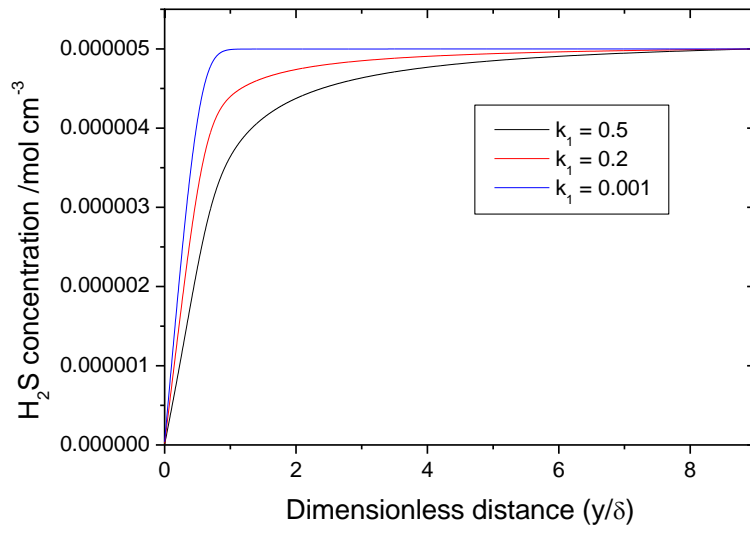


Figure 9

1 Corrosion mechanisms in aqueous solutions containing dissolved H₂S. Part 2:
2 Model of the cathodic reactions on a 316L stainless steel rotating disc electrode.

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13

14 **Abstract**
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16

17 In H₂S containing solutions, the reduction of protons with a buffer effect contributing to the
18 transport of protons at the steel surface, is not sufficient to explain the cathodic polarization
19 curves obtained on 316L stainless steel. An additional electrochemical reaction was observed
20 and was attributed to a direct H₂S reduction. A numerical model is presented with these
21 hypotheses and a good agreement is found with the experimental data presented in a previous
22 paper. With this model it is also possible to present the concentration profiles of the different
23 species involved in the cathodic process.
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List of Symbols

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4	J_i	flux of species I, mol/cm ² s
5	k_i	rate constant of species I, mol ^{0.5} /cm ^{0.5} s
6	c_i	concentration of species i, mol/cm ³
7	E	electrode potential, V
8	$b_{c,i}$	cathodic Tafel slope, V
9	D_i	diffusion coefficient of species i, cm ² /s
10	V_x	convective transport rate in the direction normal to the electrode surface, cm/s
11	R_i	the homogeneous production rate, mol/cm ³ .s
12	ν	kinematic viscosity, cm ² /s
13	ω	angular rotation speed, rd/s
14	x	normal distance to the electrode surface, cm
15	H_i	Henry's constant for species i, mol/cm ³ .bar
16	K_j	equilibrium constant of reaction j,
17	F	Faraday's constant, 96,487 C/equiv
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1. Introduction

Corrosion in weak acid solutions often represents a more complex situation than in strong acids. It is relatively well admitted that corrosion in weak acids is usually enhanced in comparison with diluted strong acids at the same pH. A simple explanation to this fact lies in the carrier of reducible proton (H^+). In a strong acid solution, all the protons are already dissociated. Consequently, pH is a good indicator of the oxidizing power of the solution. On the other hand, a weak acid solution of similar pH still contains the same amount of H^+ , but also a reservoir of protons in the form of undissociated weak acid molecules. The oxidizing power is thus accounted for by both pH and the concentration of weak acid, with immediate consequences on the intensity of the cathodic reaction at a given potential. In acid solution, H^+ reduction is often the major source of cathodic current. In a weak acid solution, this cathodic reaction is both fed by H^+ diffusion from the bulk, but also by the diffusion of the weak acid and its subsequent dissociation, in a so called buffer effect. The increase of cathodic current associated with this buffer effect is therefore seen as soon as a H^+ diffusion limitation is reached, and the higher the weak acid concentration is, the higher the increase of cathodic current. However, in order to explain the increase of cathodic current, the hypothesis of electroactivity of the weak acid is also often proposed. The direct reduction of the weak acid is then mathematically added to proton reduction, thus increasing the total cathodic current density.

Although the differences between those two mechanisms might seem subtle, major differences have to be pointed out. The buffer effect arises purely from chemical equilibriums and kinetics, without potential dependence. Another contribution has therefore to be considered. However, this contribution starts only in the potential region where H^+ reduction is under mass transport control: the weak acid then acts as a buffer, and is transported from the bulk to the electrode surface, where it dissociates to generate H^+ in situ. As a consequence, cathodic polarization curves are expected to remain unchanged in the H^+ charge transfer region, while the diffusion limited plateau must be increased with amplitude corresponding to diffusion of the weak acid.

On the contrary, a direct reduction has a strong dependence on potential. It may or it may not be found in the potential range of H^+ reduction, depending on the nature of the electrode, the nature of the weak acid and its concentration. When the contribution of weak acid reduction is not negligible, it thus presents its own current – potential characteristics with charge transfer and mass transfer limited regions, which are superimposed to H^+ reduction, enhanced by the buffer effect which is still present. If both reduction reactions have distinct potential regions and not too dissimilar current densities, two distinct electrochemical waves should be observed in the current – potential curves.

In oil and gas environments, three major weak acids are encountered: from the strongest to the weakest, organic acids, with acetic acid (CH_3COOH) as the main component, carbonic acid (H_2CO_3) and hydrosulfuric acid (H_2S). While it is known from decades that these acids strongly enhance the corrosion rates of mild steel [1-13] the level of understanding differs widely between them. CO_2 corrosion has probably benefited the widest and earliest investigations, and it is known from long that the increase of corrosion rate is associated with an increase of cathodic current density [4,5,7,9-12]. While direct reduction of H_2CO_3 remained the most often cited mechanism until the late 2000's, a recent consensus seems adopted on the buffer effect which was first proposed in 1974 [12]. This mechanism was recently confirmed by a reactive transport model showing that no additional reduction reaction was necessary to describe cathodic reactions in CO_2 solutions [14]. Similarly, recent

1 studies on acetic acid corrosion also showed that a direct reduction was not likely [15], also
 2 confirming older thoughts [3].

3 On the other hand, studies on H₂S corrosion were mainly focused on anodic mechanism or on
 4 the formation of FeS scale formation [8,16-19]. Electrochemical aspects of H₂S benefited
 5 much less investigations, though it was found to have strong impact on the cathodic current
 6 density [1,8,20]. Recent electrochemical investigations were thus performed using well
 7 controlled hydrodynamic systems and show that H₂S contribution might not fully be
 8 explained by a buffer effect [21,22].

9 In Part 1 of this paper, an electrochemical model for the cathodic reactions in H₂S solutions
 10 was proposed [21]. Buffer behaviour similar to CO₂ was first considered, where H₂S
 11 contributes through its dissociation reactions as an additional source of protons at the
 12 corroding surface:
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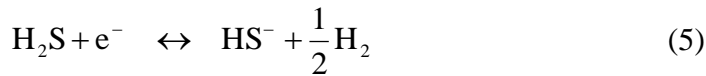
16 As in the case of CO₂ [23], it is not postulated that these reactions always stand at
 17 thermodynamic equilibrium. It could thus be necessary to consider the chemical kinetics
 18 expressions:
 19

$$20 \quad R_1 = k_1 c_{\text{H}_2\text{S}} - k_{-1} c_{\text{HS}^-} c_{\text{H}^+} \quad (3)$$

$$21 \quad R_2 = k_2 c_{\text{HS}^-} - k_{-2} c_{\text{S}^{2-}} c_{\text{H}^+} \quad (4)$$

22 where R_1 , k_1 and k_{-1} are respectively the rates of the reaction and the forward and backward
 23 kinetic constants for H₂S dissociation (Reaction (1)), and where R_2 , k_2 and k_{-2} have the same
 24 meaning for HS⁻ dissociation (Reaction (2)). Although the kinetic rate constants for these
 25 reactions are not well documented in the literature, it is often postulated that the dissociation
 26 of H₂S is much faster than for CO₂ [24].

27 As it was also shown in [21], the buffer effect is not sufficient to explain the experimental
 28 cathodic curves: an additional electrochemical reaction was observed at higher cathodic
 29 potential, which could not be represented by the proton reduction after weak acid transport
 30 and dissociation. The hypothesis of a direct reduction reaction was then considered as
 31 proposed by Bolmer [1]:
 32



34 The reaction order of this last reaction was experimentally determined in [21] and a value of
 35 0.5 was found as for the proton reduction.

36 Finally the expression of the current density for the reaction (3) was obtained after the
 37 determination of the Tafel slope:
 38

$$39 \quad J_{\text{H}_2\text{S}} = k_{\text{H}_2\text{S}} c_{\text{H}_2\text{S}}^{0.5}(0) I 0^{\frac{-E}{b_{c,\text{H}_2\text{S}}}} \quad (6)$$

40 where $k_{\text{H}_2\text{S}}$ is the cathodic rate constant of H₂S reduction, $c_{\text{H}_2\text{S}}(0)$ is the H₂S concentration at
 41 the electrode surface, E is the electrode potential, and $b_{c,\text{H}_2\text{S}}$ is the cathodic Tafel slope equal
 42 to 145±10mV [21].
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2 Governing equations

Generally, the solution under investigation contains different ions as Na^+ , SO_4^{2-} , Cl^- and then in this approach the migration is neglected. The migration can play a significant role only if H_2S is considered in pure water which is not realistic in oil and gas industry.

The governing equations of the system are the mass balance equations expressed for each species i of the model. These equations can be written according to:

$$-D_i \frac{\partial^2 c_i}{\partial x^2} + V_x \frac{\partial c_i}{\partial x} = R_i \quad (7)$$

with D_i the diffusion coefficient of species i , c_i its concentration, V_x the convective transport rate in the direction normal to the electrode surface, and R_i the homogeneous production rate, determined from (3) and (4) with the following relations:

$$R_{\text{H}^+} = R_1 + R_2 \quad (8)$$

$$R_{\text{H}_2\text{S}} = -R_1 \quad (9)$$

$$R_{\text{HS}^-} = R_1 - R_2 \quad (10)$$

$$R_{\text{S}^{2-}} = R_2 \quad (11)$$

According to Levich [25], the convective term for a rotating disc electrode can be expressed as:

$$V_x = -0.51\nu^{-1/2} \omega^{3/2} x^2 \quad (12)$$

Where ν is the kinematic viscosity of the solution, ω is the angular rotation speed of the electrode, and x is the normal distance to the electrode surface.

The complete system is described by a set of four coupled non linear differential equations (7), to solve it, the boundary conditions at the interface and in the bulk of the solution must be defined.

2.1 Boundary conditions in the bulk of the solution:

Far from the electrode, it is reasonable to consider that thermodynamic equilibrium is reached. Thus for a given pH and a given partial pressure of H_2S ($P_{\text{H}_2\text{S}}$), the bulk concentration can easily be calculated as:

$$c_{\text{H}_2\text{S}} = H_{\text{H}_2\text{S}} P_{\text{H}_2\text{S}} \quad (13)$$

$$c_{\text{HS}^-} = K_1 \frac{c_{\text{H}_2\text{S}}}{c_{\text{H}^+}} \quad (14)$$

$$c_{\text{S}^{2-}} = K_2 \frac{c_{\text{HS}^-}}{c_{\text{H}^+}} \quad (15)$$

where H_{H_2S} is the Henry's constant for H_2S , and K_1 and K_2 are respectively the equilibrium constant of Reaction (1) and Reaction (2).

It appears that $c_{S^{2-}} = K_1 \cdot K_2 \frac{C_{H_2S} \cdot C_{HS^-}}{C_{H^+}^2}$ and the corresponding value is very small, then for the pH value under investigation (pH = 4 and pH = 6, the concentration in S^{2-} is negligible and the homogeneous reaction (2) can be ignored in the present work.

2.2 Boundary conditions at the electrode surface:

At the electrode surface the flux of non electroactive species is necessarily equal to zero:

$$\left. \frac{\partial c_{HS^-}}{\partial x} \right|_{x=0} = \left. \frac{\partial c_{S^{2-}}}{\partial x} \right|_{x=0} = 0 \quad (16)$$

The electroactive species are H^+ and H_2S , then:

$$D_{H_2S} \left. \frac{\partial c_{H_2S}}{\partial x} \right|_{x=0} = J_{H_2S} \quad (17)$$

$$D_{H^+} \left. \frac{\partial c_{H^+}}{\partial x} \right|_{x=0} = J_{H^+} \quad (18)$$

J_{H_2S} is given by the expression (6) and the expression for J_{H^+} is similar and given in [21]. The boundary conditions (17) and (18) linked the concentration at the electrode to the concentration gradient.

3 Numerical solutions

3.1 Current-potential curves

Due to the product of concentrations $C_{HS^-} \cdot C_{H^+}$ in equation (3) the system is non linear. Only the equilibrium constant K_1 is tabulated but k_1 is unknown and can be determined by comparison between the numerical derivation and the experimental data. The corresponding values k_1 is deduced from the values of k_1 ($k_1 = K_1/k_1$).

The numerical value for the overall current is:

$$j = F(J_{H_2S} + J_{H^+}) \quad (19)$$

The dissociation of HS^- is neglected, the system is then reduced to three differential equations with three unknowns and only k_1 must be determined.

The stationary cathodic polarization curves measured with a rotating disc electrode at pH 4 in H_2S saturated (9 mbar) solution is recalled in Figure 1 at 600 rpm. Two waves can be clearly seen and are attributed to the reduction of the proton and to the reduction of H_2S (reaction (5)). For potentials more cathodic than -1 V, a third wave can be observed corresponding to the water reduction and is not considered in the present simulation.

1 The parameters corresponding to the simulation presented in Figure 1 are given in Table 1.
2 The results of the derivation are also given in Figure 1, a good agreement between the
3 experimental data and the simulation is obtained. The wave corresponding to the H₂S
4 reduction is obtained by taking a value for k_{H_2S} lower than the value of k_{H^+} (see Table 1).

5 In order to characterize in more details the electrochemical reactions associated with H₂S,
6 additional experiments were performed in [21] with different P_{H_2S} or less acidic solutions. All
7 simulations are obtained with the same set of coefficients (Table 1).

8 At pH 4 for 9 and 50 mbar of H₂S, the additional contribution to the proton reduction appears
9 on the polarization curves of Figure 2. For 1 mbar only the reduction of the proton appears
10 clearly. As in Figure 1 the agreement between the simulated curves and the experimental data
11 is satisfactory.
12

13 At pH 6 for the different concentrations in H₂S, the cathodic contribution of the polarization
14 curves can be attributed to H₂S and to the water reduction. The simulation confirms that the
15 limiting plateau is proportional to the H₂S concentration, but the water reduction is not
16 introduced in the model (Figure 3).
17

18 The stationary cathodic polarization curves in the limiting current domain are plotted in
19 Figure 4 for different rotation rates of the electrode at pH 6 and with 50 mbar H₂S. The
20 simulated curves show a good agreement for the kinetic part but a clear discrepancy in the
21 limiting current region. Only the curve at 180 rpm is in agreement with the experimental data.
22 The limiting cathodic current is plotted versus the square root of the rotation speed in Figure 5.
23 On this figure the simulated points corresponding to the previous curves are reported with a
24 black square, and correspond to a k_1 value of 0.2. The simulated points are below the Levich
25 plot and the corresponding curve is parallel to the Levich curve. To see the effect of k_1 on the
26 simulated results, for the same conditions the current was simulated with a k_1 value of 0.5.
27 Again the corresponding curve is below the Levich curve but always parallel to the Levich
28 curve. The experimental data follow a completely different behaviour; the increase of the
29 current with the rotation speed is much lower than the square root of the rotation speed. To
30 understand the effect of k_1 on the limiting current, in Figure 6 the limiting current
31 corresponding to a rotation speed of 180 rpm for a solution at pH 6 and with 50 mbar H₂S is
32 plotted versus the k_1 value. Clearly the value of k_1 plays an important role for k_1 around 0.1
33 and in order to obtain the best agreement on Figure 1 a value of 0.2 was chosen. The
34 homogeneous reaction (1) influences the limiting current if the k_1 value is larger than 0.01.
35 For k_1 value below 0.01 the current follows the Levich law and the homogeneous reaction
36 plays no role on the limiting current value.
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43 3.2 Concentration profiles

44 The previous model needs to derive the concentration field near the electrode for each species
45 involved in the reaction. An example of the concentration variation versus the normal distance
46 of the electrode is given in Figure 7. The distance is dimensionless by using the diffusion
47 layer thickness corresponding to the proton. In Figure 7 it appears clearly than in mixed
48 kinetic for H₂S (potential = - 0.83 V) the concentration at the interface is not zero but at this
49 potential the reduction of H⁺ is mass transport limited and the concentration at the interface is
50 zero. It appears also that the concentration gradient of HS⁻ at the interface is equal to zero in
51 agreement with the boundary conditions.
52

53 In Figure 8, the concentration profiles are presented for a potential corresponding to the
54 limiting current of H₂S. In the coordinates used in this figure, the difference between the
55 thickness of the diffusion layer for the proton and for H₂S appears clearly; this difference is
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1 obviously due to the difference between the diffusion coefficients of the two species. The HS^-
2 concentration is too small in this representation to be visible on this figure.

3 Finally, the effect of the forward constant k_f on the concentration profile of H_2S is represented
4 in Figure 9. In agreement with figure 6, the concentration profile for a k_f value small enough
5 tends towards the concentration profile without any homogeneous reaction, and for higher
6 values of k_f the concentration gradient at the interface decreases. It is interesting to notice that
7 the H_2S concentration reaches the bulk concentration at distance 6 or 7 times larger for k_f
8 equal 0.5 than for k_f equal 0.001. As consequence for large value of k_f the numerical
9 integration of the mass balance equation must be performed on a larger distance.

11 4 Discussion

12 As shown experimentally in part 1 of this paper [21], and also observed in [22], the hydrogen
13 evolution in an oxygen free solution with dissolved H_2S is different from that observed with
14 dissolved CO_2 , even though both dissolved gasses are weak acids with comparable solubility
15 and pKa. In the pH region of interest for oil and gas environments, typically between 4 and 6,
16 the concentration of dissolved acid gases (CO_2 and H_2S) is usually several orders of
17 magnitude higher than the concentration of proton. Electrochemical reactions at the steel
18 surface are then under strong influence of the transport of the weak acids coupled with their
19 dissociation. However, while this reactive transport scheme with proton reduction as unique
20 cathodic contribution was sufficient to describe polarisation curves in carbonic acid solutions,
21 the same model could not be applied satisfactorily with H_2S . As shown by numerical results
22 presented in this paper, the buffer effect is not sufficient to explain cathodic polarization
23 curves measured in solutions with dissolved H_2S . The hypothesis of an additional reduction of
24 H_2S was considered and the numerical curves are in good agreement with the experimental
25 ones. However a discrepancy appears for the variation of the limiting current with the rotation
26 speed, in contradiction with experimental results of [22], obtained with mild steel electrode.
27 Several hypothesis might be proposed to explain this discrepancy. Sulfide adsorbates at the
28 electrode surface might have disturbed the system, inducing areas with distinct
29 electrochemical reactivities. Thus, the additional electrochemical wave might be linked with a
30 second " H_2S modified surface" rather than with, or in addition to, a second electroactive
31 species. This reaction scheme is also in good agreement with the current understanding of the
32 impact of H_2S on hydrogen charging in steel, considering proton reduction through HS^-
33 adsorbate [26].

34 Another type of surface disturbance might also explain the experimental variation of the
35 limiting current with the rotation speed. This difference could be due to the fact that the direct
36 corrosion of iron with H_2S and the formation of a corrosion deposit were not taken into
37 account in the present model [18].

38 Although it is not possible to conclude at this stage, it seems also that these hypotheses
39 strongly depend on the electrode material. While we used stainless steel for its relative
40 inertness for this investigation, carbon steel presents a much greater practical interest, and
41 constitutes the main perspective to this work. In particular, the rapid formation of corrosion
42 scales is expected, constituting a porous diffusion layer. The model could then be modified in
43 order to remove the convective transport contributions, and apply a diffusion layer in the
44 typical range of corrosion scales, from tens of micrometres to millimetres. This will also
45 require taking account of ferrous ions diffusions from the steel surface through the porous
46 layer, and also consider precipitation reactions. This model could then be applied to discuss
47 corrosion under deposit mechanisms as described in [27,28]. Such mechanistic models of CO_2
48 and H_2S underdeposit corrosion already exist, but they do not incorporate actual
49 understanding of H_2S electrochemistry and reactive transport [19].
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1 Improving the understanding of H₂S corrosion of carbon steel would also be valuable for
2 hydrogen cracking applications, with a better understanding of the impact of adsorbates on
3 hydrogen entry.

4 **5 Conclusions**

7 The contribution of H₂S to cathodic reactions differs from that of CO₂ or acetic acid. In the
8 latter case, proton reduction is the main cathodic reaction, and dissolved CO₂ or acetic acid
9 only contribute to increase the current density in the mass transfer control potential range by a
10 chemical buffer effect. While such buffer effect still holds with H₂S, it is no more sufficient to
11 explain the rise of cathodic current, and the appearance of a second electrochemical wave. A
12 kinetic model, including both a buffer effect and a direct H₂S reduction was proposed in Part
13 1 of this paper. Numerical resolution was proposed in this paper, and showed good agreement
14 with experimental data obtained on a 316L rotating disc electrode in pH region 4 to 6 and H₂S
15 partial pressure from 1 to 50 mbar.
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Figure captions

Fig 1 : Stationary cathodic polarization curves measured with a RDE at pH 4 in 9 mbar H_2S saturated solution for a rotation speed of 600 rpm. The simulated points are obtained by solving the set of three differential equations (7).

Fig 2 : Stationary cathodic polarization curves measured with a RDE at 180 rpm in de-aerated solution containing different amount of H_2S at pH 4. The simulated points are obtained by solving the set of three differential equations (7).

Fig 3 : Stationary cathodic polarization curves measured with a RDE at 180 rpm in de-aerated solution containing different amount of H_2S at pH 6. The simulated points are obtained by solving the set of three differential equations (7).

Fig 4 : Experimental stationary cathodic polarization curves measured with a RDE at different rotation speed in de-aerated solution containing at pH 6 with 50 mbar H_2S .

Fig 5 : Evolution of the limiting cathodic current with the rotation speed of the electrode in de-aerated solution at pH 6 with 50 mbar H_2S . The line represents the theoretical Levich law for H_2S and the different square the simulated points with different values of the parameter k_1 .

Fig 6 : Variation of the limiting current in function of the k_1 value for a solution at pH 6 with 50 mbar H_2S and a rotation speed of 180 rpm.

Fig 7 : Concentration profiles for the three species in mixed kinetic ($E=-0.83$, pH = 4, $\Omega = 180$ rpm, $P_{H_2S} = 9$ mbar)

Fig 8 : Concentration profiles according to the normal dimensionless distance to the electrode for a potential corresponding to the limiting current plateau of H_2S .(pH = 4, $\Omega = 1200$ rpm, $P_{H_2S} = 1$ mbar)

Fig 9 : Concentration profiles of H_2S for different k_1 values.(pH = 6, $\Omega = 180$ rpm, $P_{H_2S} = 50$ mbar)

Table caption

Table 1: *Values of the constant used for the calculation ($T = 25^{\circ}\text{C}$). Remark the difference between the value of k_{H^+} given in this table and in [1] is due to the difference of reference electrode used in [1] (SSE and in the present work (Ag/AgCl)).*

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Reviewer #1:

This work is well done and can be accepted to be published in the special issue of EA dedicated to the EMCR 2012. However, I have two comments about the paper: 1- The figures 7 and 8 were obtained without take into account the migration and consequently the electroneutrality equation. In the author point of view these curves will change significantly taking into account the global problem?

Reply: We do not consider in this paper solutions of pure water without dissolved salts, for which migration effect could be expected, as mentioned by the reviewer.

A sentence was added at the beginning of §2 to indicate that migration was not taken into account, and the justification for that.

> 2- I propose to the authors to add a list of symbols. It is easier for the reader.

Reply: A list of symbols was added

Reviewer #2:

The reviewer has read the paper with interest, finds the topic to fit well in the scope of ElChimActa, finds the results and discussion of them presented scientifically sound, but on the other hand finds the overall length and content of the paper on the lean side. The reviewer would suggest to check whether this proposed Part 2 can be combined with the Part 1 manuscript of this mini-series, possibly by combining/merging separate Figures of this now-Part 2. If found not feasible (and also when merged with Part 1), this Part 2 paper format and structure should at least be reconsidered:

1 - The Introduction has 10 references only, of which 2-6 are referred to in bulk. The Introduction should present the state-of-the-art in this research field and its current form is very unsatisfactory and does not lead to a clear aim on how this particular work reaches beyond this state-of-the-art and a clear statement which 'novel' approach is followed to get there is needed. The limited number of references to prior literature are and do not represent a proper context for this work. Discussion of prior literature does not reach beyond a very general and basic level. To not discuss individual prior contributions to the research field in detail and how the authors do fill in the gaps in prior literature means that the authors have not done due diligence, and not crafted a paper as critical as it could be, as yet.

Reply:

The introduction was deeply improved, to give a clearer view of state-of-the-art, and explain more precisely the 'novel' approach proposed in this paper. The number of references was increased significantly, without excessive bulk citations. Emphasis is given in the comparison between well known areas, i.e. CO₂ and acetic acid electrochemistry, and H₂S, which is the main subject of this paper.

We have the feeling that self-consistency of this part 2 is greatly improved, and are grateful to the reviewer for his constructive comments.

2 - the Conclusions paragraph is now about one A4 in length, even including parts of a discussion of results, speculation, recommendations for future work and moreover still references to prior literature (which should be done in a Discussion part). The Conclusions paragraph should be short and crisp and the majority of the now-Conclusions part should be spliced into the Discussion part.

Reply:

We fully agree with the comments by the reviewer. The previous conclusion was more in the format of a discussion. A discussion § paragraph 4 was then added, with the text of previous conclusion.

A new and shorter conclusion is proposed, to summarize the main findings of the work.

3 -The reviewer suggests to put at least 'steel surfaces' in the title to reflect the modeling of the cathodic reactions on steel surfaces as referred to many times in the actual manuscript text.

Reply: Title was modified to mention 'on a 316L rotating disc electrode', similarly to part 1 of the paper.