General corrosion is the main form of corrosion likely to affect carbon steels in an anoxic and near neutral environment such as encountered in the context of long term storage of steel canisters in a deep geological repository. This paper aims at studying the influence of the electrical and geometrical properties of a siderite corrosion product layers (CPL) formed in such conditions on its stability and on its subsequent protective properties against corrosion. A 1-D numerical model describing general corrosion under a porous conductive CPL and accounting for chemical evolution in the electrolyte is presented. It is demonstrated that a conductive layer with a cathodic activity increases the corrosion rate and the Fe$^{2+}$ ions concentration. Otherwise, a conductive layer leads to high saturation levels of siderite and high pH values within the CPL and consequently to a stabilization of the CPL. It is shown also that the stability of the CPL is promoted when it is initially thick and/or when it has a low porosity.

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In the context of geological disposal of High Level radioactive Waste (HLW) over several thousand years it is necessary to predict long term corrosion of the metals in contact with liquid or solid phases present in the geological environment. In France, these HLW would be stored in a near neutral deep Callovo-Oxfordian (Cox) argillite, and low alloyed steel will be used for most of the metal components (overpack, liner) in contact with this environment.1

In this context, different corrosion steps are expected: a dry corrosion step during operated phase, a step of aqueous corrosion under oxidizing conditions (oxygen reduction) and a step of aqueous corrosion under anodic conditions. This latter step, much longer than the first ones, is considered in our research. During this phase, in the absence of passivation, the main form of corrosion likely to affect carbon steels is general corrosion leading to the formation of a thick corrosion product layer (CPL) mainly composed of siderite (FeCO$_3$) in an argilligous environment.2 Then, predicting corrosion evolution of steel components in contact with the Cox environment necessitates to account for the role and properties of this siderite CPL. It must be emphasized that the formation of siderite CPL have been considered in some numerical models to predict the evolution of general corrosion occurring on carbon steel in acidic (CO$_2$ and/or H$_2$S) environments in the petroleum context, using either an empirical / semi-empirical approach3–5 or mechanistic models.6–10

In a near neutral environment in the field of HLW repository, semi-empirical models based on experiments,11,12 and mechanistic models13–17 have also been developed to predict the evolution of the corrosion rate of carbon steel.

Furthermore, the role of the CPL has been highlighted and implemented in their models by other authors.18–22 However, the electrical properties of the CPL were not implemented. The CPL was only considered as an additional diffusive barrier. For instance, King used a fixed porosity coefficient, characteristic of the CPL, in the transport equations16,21,22 and Nesic et al. defined a porosity coefficient for the CPL function of time and distance from the steel surface.20

In a previous study carried out in the context of radioactive wastes repository the estimation of the corrosion rate evolution of carbon steel has been performed based on a numerical approach in which the effect of the CPL was considered in terms of a porosity decrease.23 This previous study also permitted to identify the suitable kinetics parameters to be used in this context.

It is worth noting that the role of the CPL is not limited to a diffusive barrier or to a uniform limitation of the transport of all species. Crolet studied the role of the diffusion mechanism through the CPL on its protectiveness.24 The main result of Crolet is that depending on which ions (Fe$^{2+}$ or CO$^{2-}$ in the case of a siderite CPL) will be firstly impeded to diffuse by the growing CPL, ones might obtain either a protective or a non-protective CPL referred by I$_{c}$ (cathodic) and I$_{a}$ (anodic) respectively. Consequently, the decrease of the corrosion rate is not at all related to the CPL growth step. Otherwise, Crolet investigated the role of the electrical properties of the CPL on the corrosion rate of carbon steel15–22 assuming that a conductive CPL can increase the corrosion rate of carbon steel and lead to an internal acidification within the CPL next to the metal surface resulting from the bicarbonate depletion. Indeed, experimental results obtained by Necib et al.25 have shown cases of protective CPL and cases of non-protective CPL that could result from an initial acidic and aerated transient of the environment.

In the present paper, we focus on the influence of the electrical properties of the CPL on its stability and on its ability to reduce the corrosion rate of carbon steel. To our knowledge only Venkattraman et al.31 proposed a 1-D numerical model of general corrosion under a conductive layer. This model allows simulating the cathodic contribution of the porous layer residing on the metal surface under various situations. In their approach the cathodic contribution supplied by the CPL led systematically to an increase of the corrosion rate since the chemical evolution inside the electrolyte was not taken into account in their model.

In a carbonate environment, carbon steel (especially pearlitic) dissolution can leave a conductive cementite skeleton in electrical contact with the metal.26–30 In this study, the cementite is to be mixed with the siderite leading to a conductive CPL. This new conductive phase could affect the corrosion rate at different levels (i) acting as a diffusion barrier for electroactive species, and then promoting CPL precipitation when its saturation threshold is reached, (ii) increasing the cathodic activity and consequently the corrosion rate. It is also worth mentioning that the conductive surface area of the CPL must be lower than the specific surface of the CPL itself since only a skeleton of cementite inside the CPL is supposed to be conductive.

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A FeCO₃ CPL with constant thickness and porosity is assumed and the stability of this CPL is deduced from the profile evolution of the saturation level of siderite (FeCO₃) which is expected to be the only solid to precipitate.² Otherwise, regarding the initial chemical composition, Fe(OH)₂₈ is always undersaturated in our simulations at T = 25°C (the temperature is kept equal to T = 25°C). The pore water contains the following chemical species:¹⁻²È carbonate and then limiting the corrosion rate. It is therefore not easy to predict whether the presence of a conductive CPL promotes, or not, the protectiveness of the carbon steel. A numerical approach accounts for the effect of conductivity of the CPL on its protectiveness. This concept of protectiveness of the CPL and its stability was first introduced by Van Hummik et al. in terms of a scaling tendency (ST) to account for the effect of the CPL.¹⁹ In a modelling approach,¹⁰,²⁰ this ST factor has been used and expressed as depending on the ratio of corrosion rate and precipitation rate of corrosion products.

The model accounts for chemical evolution in the electrolyte (diffusion layer) and is based on the porous electrode theory developed by Newman.³²⁻³⁵ Once considering a conductive CPL, the porous electrode theory is adapted in this work to study the evolution of the stability of a CPL by modifying both the electrical parameters and the morphological parameters of the CPL. The influence of stable Fe(II) complexes is also studied.

### Governing Equations

**Conceptual model and general assumptions.**—The numerical modelling is a 1-D numerical model (Figure 1) of general corrosion under a porous and more or less conductive CPL.

**Figure 1.** Schematic representation of a CPL present at the initial state. The initial CPL thickness (e = L) and porosity (ε = a) are the input data.

This paper deals with this last effect. It is expected that the presence of a porous conductive layer on the metal surface should lead to an increase of the corrosion rate and of the pH within the CPL resulting from an increase of the cathodic contribution, promoting the precipitation of corrosion products such as metal hydroxide or carbonate and then limiting the corrosion rate. It is therefore not easy to predict whether the presence of a conductive CPL promotes, or not, the protectiveness of the carbon steel. A numerical approach accounting for a conductive CPL is then necessary to assess the effect of the conductivity of the CPL on its protectiveness. This concept of protectiveness of the CPL and its stability was first introduced by Van Hummik et al. in terms of a scaling tendency (ST) to account for the effect of the CPL.¹⁹ In a modelling approach,¹⁰,²⁰ this ST factor has been used and expressed as depending on the ratio of corrosion rate and precipitation rate of corrosion products.

The main objective of this numerical study is to assess the impact of the electrical properties of the CPL (conductivity, contact resistance) and its geometrical parameters (thickness, reactive surface area, porosity) on its stability and on the subsequent evolution of the corrosion rate.

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### Table I. Initial concentration (mol/L) of the system. TIC stands for the total inorganic carbon concentration.

|    | H⁺ | OH⁻ | Ca²⁺ | Na⁺ | Cl⁻ | TIC | CO₂(aq) | HCO₃⁻ | CO₃²⁻ |
|---|---|---|---|---|---|---|---|---|---|
| 10⁻⁷.² | 10⁻⁶.⁸ | 8.0.10⁻³ | — | 0.026 | 0.041 | 2.1.10⁻³ | 4.45.10⁻⁴ | 1.65.10⁻³ | 2.13.10⁻⁶ |

### Table II. Homogeneous chemical reaction.

| Reaction | Rate | Homogeneous reaction | log K at 25°C |
|---|---|---|---|
| Rₛ₁ | k₄₁f, aCO₂ → k₄₁b, aH⁺ | CO₂(aq) + H₂O ⇌ HCO₃⁻ + H⁺ | -6.63 |
| Rₜ₂ | kₜ₂f, aHCO₃⁻ → kₜ₂b, aCO₂⁻ | HCO₃⁻ + H₂O ⇌ CO₃²⁻ + H⁺ | -10.09 |
| Rₜ₀ | kₜ₀f - kₜ₀b, aOH⁻ → aH⁺ | H₂O ⇌ OH⁻ + H⁺ | -14 |
| Rₜ₁| kₜ₁f, aFeOH⁺ → kₜ₁b, aFeOH⁻ | Fe²⁺ + H₂O ⇌ FeOH⁺ + H⁺ | -9.5 |
As shown in Figure 2, steel corrosion occurs under a porous medium, where the transport phenomena inside the electrolyte domain (see below for the transport in porous media) is solved using a finite element method (FEM). As shown in Figure 1, a 1-D model is considered with a first node \( \Gamma_1 \) corresponding to the metal-CPL interface and a second node \( \Gamma_2 \) corresponding to the end of the system. The length of the domain (distance between nodes \( \Gamma_1 \) and \( \Gamma_2 \)) is equal to 1 mm. An optimized and uniform meshing is used for the domain: the mesh is very tiny (1 \( \mu \text{m} \) width) and we obtain 1000 meshes. The values of the parameters used in the numerical model are summarized in Table V.

**Model and governing equations for the porous electrode theory.**—As shown in Figure 2, steel corrosion occurs under a porous and conductive CPL. The liquid phase is characterized by an electrical potential \( \psi_L \) and an electrical current density \( i_L \), and the solid (CPL) phase by \( \psi_c \) and an electrical current density \( i_c \). The transport equations in conductive porous media are based on the theory of porous electrode developed by Newman and mainly applied to batteries. Newman’s approach relies on a homogenization of the set of variables. The variables are systematically averaged through the porous layer. Details on geometry (porosity, tortuosity) are not considered. Thus, the kinetics of the reactions taking place within the pores are expressed in terms of current transfer per unit volume. The charge transfer between the liquid phase and the porous CPL is given by equations 5a–5b (in bold to designate the vectors). The index “d” refers to the deposit (CPL).

\[
\nabla \cdot \mathbf{i}_L = -S_p \left( i^d_{c,HCO_3} + i^d_{c,H_2O} \right) \quad [5a]
\]

\[
\nabla \cdot \mathbf{i}_c = -S_p \left( i^d_{c,HCO_3} + i^d_{c,H_2O} \right) \quad [5b]
\]

with \( S_p \) the specific surface area of the conductive phase in the CPL expressed in \( \text{m}^{-1} \) and depends on the total specific surface area \( S_s \). The value of this specific surface area is expressed as a function of the porosity \( \epsilon_L \) which is supposed constant. Assuming cylindrical pores (with a radius \( r \)) perpendicular to the metal surface the specific surface area is given by:

\[
S_p = \frac{2(1 - \epsilon_L)}{r} \quad [5c]
\]

**Table III.** Electrochemical reaction occurring at the metal surface.

| Reaction | cathode reaction | anode reaction |
|----------|-----------------|----------------|
| \( Fe \rightarrow Fe^{2+} + 2e^- \) | | |
| \( 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \) | | |
| \( 2HCO_3^- + 2e^- \rightarrow H_2 + 2CO_2^- \) | | |

Expressed through the Nernst–Einstein equation: \( u_i = D_i / RT \), where \( T \) is the absolute temperature (K) and \( R \) the universal gas constant \( (R = 8.314 \text{ J mol}^{-1} \text{K}^{-1}) \).

Then, the electroneutrality condition is assumed:

\[
\sum_i z_i C_i = 0 \quad [4]
\]

**Table IV.** Electrochemical reaction occurring at the CPL surface.

| Reaction | cathode reaction | anode reaction |
|----------|-----------------|----------------|
| \( 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \) | | |
| \( 2HCO_3^- + 2e^- \rightarrow H_2 + 2CO_2^- \) | | |

The transport equations in conductive porous media are based on the theory of porous electrode developed by Newman and mainly applied to batteries. Newman’s approach relies on a homogenization of the set of variables. The variables are systematically averaged through the porous layer. Details on geometry (porosity, tortuosity) are not considered. Thus, the kinetics of the reactions taking place within the pores are expressed in terms of current transfer per unit volume. The charge transfer between the liquid phase and the porous CPL is given by equations 5a–5b (in bold to designate the vectors). The index “d” refers to the deposit (CPL).

**Table V.** Values of the parameters used in the numerical model.

| Parameter | Value |
|-----------|-------|
| Consistent initialization of differential equation system | Backward Euler |
| Solver | PARDISO |
| Implicit method of resolution | BDF (Backward Differentiation Formulas) |
| Order of accuracy: min – max | 1-2 |
| Time interval | 0-10^8 s |
| Relative tolerance | 10^{-3} |
| Absolute tolerance | 10^{-3} |
| Mesh | Free Mesh, Edge |
| Type of elements | Edge |
| Order | 2s Order |
| Size | 1 \( \mu \text{m} \) |
| Number of elements | 1000 |
| Variable time step | 10^9, with x \( \in [0.8] \) |
| Step | 0.1 |
| Initial step | 10^{-3} |
| Maximum step | 10^9 |

![Figure 2](image-url) Schematic representation of corrosion reactions under a conductive CPL (\( \epsilon = \epsilon_L \)). The surface of the metal is at \( x = 0 \). The porous domain with the electrolyte is represented according to two domains: liquid phase (pore) and a solid phase (CPL). The motion of the electrons is shown by the dotted line (red) and the current densities are represented by the black arrows. The dashed arrows (blue) represent the transport of species from (and to) the bulk to (and from) the surface of the metal.
It is worth noting that the conductive surface “$S_p$” must be lower than the specific surface of the CPL ($S_L$). The driving force of the current density “$i^d$” is given by the potential difference between the solid and the liquid phase (i.e. $\phi_s - \phi_L$) within the CPL as depicted in Figure 2.

The potential distribution in the CPL is related to the current local density by Ohm’s law:

$$i = -\sigma_r (1 - \epsilon_L) \nabla \phi_i$$  \[6\]

with “$\sigma_r$” the conductivity of the CPL (S.m$^{-1}$) and “$1 - \epsilon_L$” the fraction of the solid phase taking into account the porosity of the layer.

The current in the liquid phase is due to the ionic fluxes:

$$i_1 = F \sum z_i N_i$$  \[7\]

Within the liquid phase, in the pore solution, equation 2 and Eq. 3 give the superficial flux and the mass conservation are rewritten as:

$$\nabla C_i - z_i u_{mi,eff,f} \cdot F \nabla C_i - \nabla q_L = 0$$  \[8\]

where $D_{i,eff}$, $z_i$, $u_{mi,eff,f}$ represent respectively the effective diffusion coefficient (m$^2$.s$^{-1}$), the charge number and the effective ionic mobility (s.mol.kg$^{-1}$) of species $i$ ($D_{i,eff}$ = $D_i ^{0} \ast \epsilon_L$, $u_{mi,eff,f} = u_{mi} ^{0} \ast \epsilon_L$). The term “$R_{tot}$” (Eq. 10) corresponds to the sum of the chemical reactions ($i_1$, $R_L$) taking place in the liquid phase (solution in the pores) and the reaction term (Eq. 11) due to the interfacial fluxes of species from the solid phase into the solution (due to the electrochemical activity of the conductive phase) as depicted in Figure 2 ($R^d_j$). The total reaction term is expressed in mol.m$^{-3}$.s$^{-1}$:

$$R_{tot} = \sum_j R^d_j + \epsilon_L R_i$$  \[10\]

Here “$\nu_j$” corresponds to the stoichiometric coefficient, “$m$” to the number of electrons and “$F$” to the Faraday constant. “$i^d$” corresponds to the electric current density (see Table IV). Finally, the electroneutrality is verified throughout the medium. In our case, we have two additional reaction terms due to the electrochemical activity of the CPL (bicarbonate and water reduction) given by:

$$R^d_{\text{HCO}_3^2} = \frac{S_{\text{HCO}_3^2} \cdot i^d_{\text{HCO}_3^2}}{F}$$  \[12a\]

$$R^d_{\text{CO}_2} = \frac{S_{\text{CO}_2} \cdot i^d_{\text{CO}_2}}{F}$$  \[12b\]

Table VI summarizes the model data in terms of diffusion coefficients and chemical reaction terms for each chemical species.

**Boundary conditions.**—Under free corrosion conditions, electrons generated at node $\Gamma_1$ (iron dissolution) (see Figure 2) “supply” bicarbonate and water reduction occurring on the metal and CPL surface. On the other hand, it is assumed that the contact between the metal and the CPL is ohmic thus the current flowing at any point of the CPL can be expressed by:

$$I_{n-d} = \frac{q_m - \phi_i}{\varrho_{n-d}} \cdot \epsilon_L \cdot A = i_j \cdot A \cdot (1 - \epsilon_L)$$  \[13\]

with “$q_m$” the potential of the metal surface (assumed to be equal to 0 V), “$\phi_i$” the potential of the CPL at the metal surface and “$A$” the surface of the corroding metal, also called the effective cross-sectional area. $A$ is equal to 1 m$^2$, and the porosity $\epsilon_L$ corresponds to the ratio of the metal not covered by the CPL (i.e. the active surface ratio). “$\epsilon_L$” is the scalar of the current density vector “$i_j$” and “$\varrho_{n-d}$” is the specific contact resistance between the metal and the CPL. This parameter represents a barrier for electrons moving from the metal surface to the CPL. It is supposed to reflect a possible insulating phase that could be formed between the metal surface and the conductive CPL.

At the metal – pore solution interface the current is equal to the sum of oxidation and reduction currents occurring at the metal surface:

$$I_{m-solution} = \left( i_{m,FECO_3} + i_{m,HCO_3^2} + i_{m,\text{H}_2\text{O}} \right) \cdot A \cdot \epsilon_L = i_j \cdot A \cdot \epsilon_L$$  \[14\]

with “$\epsilon_L$” the scalar of the current density vector “$i_j$”

Since there is no external current in the system, the total current is therefore equal to zero:

$$I_{m-d} + I_{m-solution} = 0$$  \[15\]

And by combining Equations 13 to 15, the electrical potential of the CPL when thickness $x$ tends to 0 is given by:

$$\phi_i = \phi_m + \left( i_{m,FECO_3} + i_{m,HCO_3^2} + i_{m,\text{H}_2\text{O}} \right) \cdot \varrho_{n-d} \cdot \frac{\epsilon_L}{1 - \epsilon_L}$$  \[16\]

At $x = L$ no current can escape from the solution or the solid phase to the bulk solution. Therefore, $i_j = i_L = 0$.

Finally, at the end of the simulated domain ($x = 1 \text{mm}$) as well as at the limit of the diffusion layer ($x = L + 500 \mu \text{m}$) a bulk concentration condition is imposed for all the chemical species: $c_i = c_0$.

**Initial conditions.**—Since the CPL is present over a certain thickness $L$ at the initial state, the concentration of $Fe^{2+}$ within the CPL at $t = 0$ s can be expressed as function of the solubility product of $FeCO_3$ and the initial carbonate concentration:

$$[Fe^{2+}]_{t=0} = \frac{K_{FeCO_3} \cdot (CO_3^{2-})^2_{t=0}}{[CO_3^{2-}]_{t=0}}$$  \[17\]

The initial concentration of carbonate depends on the initial pH and the initial total inorganic carbon (TIC) concentration. The reference concentration $CO_3^{2-}$ is equal to 1 mol/L.

**Input data.**—The influence of geometrical and electrical properties of the CPL will be addressed in a parametric study. Before this, a set of parameter values (given in Table VII) has to be fixed in a preliminary study in order to highlight the influence of a conductive CPL in comparison with an inert CPL. It should be noted that the porosity and thickness of the CPL are representative of siderite layers observed in our conditions and the electrical parameters are in the same order of magnitude as those used in Reference 31 for metal oxides.

The kinetics and thermodynamics constants summarized in Table VIII have been selected in a previous study based on a well-documented literature.

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Table VI. Chemical reaction terms for each chemical species with their respective coefficient in the bulk solution.

| Species | Diffusion coefficient (m$^2$.s$^{-1}$) | Reactions | Reactions within the CPL |
|---------|-------------------------------------|-----------|--------------------------|
| Na$^{+}$ | 1.33.10$^{-9}$ | 0 | 0 |
| Cl$^{-}$ | 2.03.10$^{-9}$ | 0 | 0 |
| Ca$^{2+}$ | 0.9.10$^{-9}$ | 0 | 0 |
| H$^{+}$ | 9.3.10$^{-9}$ | $R_m + R_{\text{FEOH}}$ | $R_{m} + R_{\text{FEOH}}$ |
| OH$^{-}$ | 5.3.10$^{-9}$ | $R_m$ | $R_{m,\text{CL}} + R_{\text{H}_2\text{O}}$ |
| $Fe^{2+}$ | 7.1.10$^{-10}$ | $-R_{\text{FEOH}}$ | $-R_{\text{FEOH}}$ |
| $FeOH^{+}$ | 7.5.10$^{-10}$ | $R_{\text{FEOH}}$ | $R_{\text{FEOH}}$ |
| $CO_{2}$ | 7.2.10$^{-10}$ | $R_{m} - R_{\text{H}_2\text{O}}$ | $(R_{m} - R_{\text{H}_2\text{O}})_L = R^d_{\text{HCO}_3^2}$ |
| $HCO_3^{-}$ | 1.9.10$^{-9}$ | $R_{m} - R_{\text{H}_2\text{O}}$ | $(R_{m} - R_{\text{H}_2\text{O}})_L = R^d_{\text{HCO}_3^2}$ |
| $CO_3^{2-}$ | 9.23.10$^{-10}$ | $R_{m}$ | $R_{m}\epsilon_L + R^d_{\text{HCO}_3^2}$ |
The stability of the CPL is evaluated through the saturation level $S_{FeCO}$ of the siderite:

$$S_{FeCO} = \frac{[Fe^{2+}][CO_3^{2-}]}{K_{s,FeCO}(CO^0)^2}$$  [18]

**Preliminary study.**—Simulations are carried out using parameter values given in Table VII.

The driving force of the additional cathodic contribution supplied by the CPL is the potential difference (Galvani Potential) $\psi_{CPL} - \psi_L$. This potential difference reaches rapidly a steady state and its value is close to the corrosion potential ($E_{corr}$) as shown in Figures 3a and 3b.

Hence, the cathodic current densities on the surface of the metal and within the CPL are quite close. However, due to the conductive specific surface area “$S$” of the CPL, the total cathodic current generated within the CPL is considerably greater than the total cathodic current generated at the surface of the metal (Figure 3c).

Figure 3d gives the profile of the current densities $i_{a}$ (solution) and $i_{s}$ (solid) at steady state at the CPL-solution interface. It is worth noting that according to Figure 3d, the linearity of the current densities implies uniformity of the cathodic activity within the CPL (see Eq. 5a).

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**Table VII. Input parameters used for the reference model.**

| Entity                              | Notation | Values     |
|-------------------------------------|----------|------------|
| CPL thickness                       | $L$      | 100 $\mu$m |
| CPL porosity                        | $\varepsilon$ | 0.1         |
| Specific surface area of the CPL Sp | $S_p$    | 10$^6$ m$^{-1}$ |
| Specific surface area of the conductive CPL | $S_r$   | 1% $S_p := 10^4$ m$^{-1}$ |
| CPL’s conductivity                  | $\sigma_r$ | 10$^{-2}$ S.m$^{-1}$ |
| Specific contact resistance         | $\rho_{m-d}$ | 10$^{-2}$ $\Omega$.m$^2$ |

**Table VIII. Summary of all the parameters: values and units.**

| Constants/Variables | Description                                                                  | Value/unit |
|---------------------|-----------------------------------------------------------------------------|------------|
| $i_{H_2O}$          | Current density for the reduction of $H_2O$                                 | $A$.m$^{-2}$ |
| $i_{HCO_3^-}$       | Current density for the reduction of $HCO_3^-$                              | $A$.m$^{-2}$ |
| $i_{Fe}$            | Apparent exchange current density for the reduction of $H_2O$               | $1.45 \times 10^{-4}$ A.m$^{-2}$ |
| $i_{H_2O}^0$        | Apparent exchange current density for the reduction of $HCO_3^-$            | $9.28 \times 10^{-5}$ A.m$^{-2}$ |
| $i_{CO_3}^0$        | Apparent exchange current density for the oxidation of $CO_2$              | $1.58 \times 10^{-2}$ A.m$^{-2}$ |
| $i_{Fe}^0$          | Apparent exchange current density for the oxidation of iron                 | $0.48 \times 10^{-2}$ |
| $i_{CO_3}^0$        | Apparent exchange current density for the oxidation of $CO_3^-$             | $0.40 \times 10^{-2}$ |
| $i_{Fe}^0$          | Apparent exchange current density for the reduction of $Fe^{2+}$            | $1.08 \times 10^{-2}$ |
| $i_{Fe}^0$          | Apparent exchange current density for the oxidation of iron                 | $5.8 \times 10^{-3}$ |
| $i_{Fe}^0$          | Electrochemical mobility of the $i^{th}$ species                          | $115.8 \times 10^{-3}$ |
| $u_i$               | Flow of the $i^{th}$ species                                                | $A$.m$^{-2}$ |
| $N_i$               | Reaction rate of the $i^{th}$ species                                       | $A$.m$^{-2}$ |
| $R_i$               | Siderity density                                                           | $mol$.m$^{-3}$.s$^{-1}$ |
| $\rho_Fe$           | Iron density                                                                | $mol$.m$^{-3}$.s$^{-1}$ |
| $M_{Fe}$            | Molar iron weight                                                          | $mol$.m$^{-3}$.s$^{-1}$ |
| $M_{FeCO_3}$        | Siderite density                                                           | $mol$.m$^{-3}$.s$^{-1}$ |
| $M_{FeCO_3}$        | Reaction rate of the autoprotolysis of water                               | $mol$.m$^{-3}$.s$^{-1}$ |
| $k_{Fe^{2+}}$       | Kinetic constant of the autoprotolysis of water (forward)                   | $10^3$mol.m$^{-3}$.s$^{-1}$ |
| $k_{Fe^{2+}}$       | Kinetic constant of the autoprotolysis of water (backward)                  | $10^{11}$mol.m$^{-3}$.s$^{-1}$ |
| $k_{FeCO_3}$        | Reaction rate of the first dissociation of dissolved $CO_2$                 | $10^6$mol.m$^{-3}$.s$^{-1}$ |
| $k_{FeCO_3}$        | Kinetic constant of the first dissociation of dissolved $CO_2$ (forward)    | $10^6$mol.m$^{-3}$.s$^{-1}$ |
| $k_{FeCO_3}$        | Kinetic constant of the first dissociation of dissolved $CO_2$ (backward)   | $10^6$mol.m$^{-3}$.s$^{-1}$ |
| $k_{FeCO_3}$        | Reaction rate of the second dissociation of dissolved $CO_2$ (forward)      | $10^6$mol.m$^{-3}$.s$^{-1}$ |
| $k_{FeCO_3}$        | Kinetic constant of the second dissociation of dissolved $CO_2$ (forward)   | $10^6$mol.m$^{-3}$.s$^{-1}$ |
| $k_{Fe^{2+}}$       | Kinetic constant of the second dissociation of dissolved $CO_2$ (backward)   | $10^6$mol.m$^{-3}$.s$^{-1}$ |
| $R_{Fe^{2+}OH}$     | Reaction rate of the hydrolysis of $Fe^{2+}$                                | $10^4$mol.m$^{-3}$.s$^{-1}$ |
| $k_{Fe^{2+}OH}$     | Kinetic constant of the hydrolysis of $Fe^{2+}$ (forward)                    | $10^{16}$mol.m$^{-3}$.s$^{-1}$ |
| $k_{Fe^{2+}OH}_b$   | Kinetic constant of the hydrolysis of $Fe^{2+}$ (backward)                   | $10^{16}$mol.m$^{-3}$.s$^{-1}$ |
| $R_{FeCl^+}$        | Reaction rate of complex $FeCl^+$                                           | $1$mol.m$^{-3}$.s$^{-1}$ |
| $k_{FeCl^+}$        | Kinetic constant of the of complex $FeCl^+$ (forward)                        | $1$mol.m$^{-3}$.s$^{-1}$ |
| $k_{FeCl^+}$        | Kinetic constant of the complex $FeCl^+$ (backward)                          | $10^{-3}$mol.m$^{-3}$.s$^{-1}$ |
| $R_{FeHCO_3^+}$     | Reaction rate of complex $FeHCO_3^+$                                        | $10^{-3}$mol.m$^{-3}$.s$^{-1}$ |
| $k_{FeHCO_3^+}$     | Kinetic constant of the complex $FeHCO_3^+$ (forward)                        | $10^{-3}$mol.m$^{-3}$.s$^{-1}$ |
| $k_{FeHCO_3^+}$     | Kinetic constant of the complex $FeHCO_3^+$ (backward)                       | $10^{-3}$mol.m$^{-3}$.s$^{-1}$ |
| $R_{FeCO_3^{aq}}$   | Reaction rate of complex $FeCO_3^{aq}$                                      | $10^{-3}$mol.m$^{-3}$.s$^{-1}$ |
| $k_{FeCO_3^{aq}}$   | Kinetic constant of the complex $FeCO_3^{aq}$ (forward)                     | $10^{-3}$mol.m$^{-3}$.s$^{-1}$ |
| $k_{FeCO_3^{aq}}$   | Kinetic constant of the complex $FeCO_3^{aq}$ (backward)                    | $10^{-3}$mol.m$^{-3}$.s$^{-1}$ |
Figure 3. a) Profile of the Galvani potential \( \phi_s - \phi_L \), b) Profile of the corrosion potential, c) Profile of the ratio between the total cathodic current (metal/CPL), d) Profiles of the superficial current densities \( i_L \) and \( i_S \) within the conductive CPL. Parameters: \( L = 100 \mu m \), \( \varepsilon = 0.1 \), \( \rho_m = 0.01 \Omega m^2 \), \( \sigma_s = 0.01 \) S/m and \( Sr = 1\% \times Sp \).

Figure 4a shows the saturation level of siderite through the whole domain. This saturation level is an indication of the tendency of the CPL to either stabilize or dissolve. Its value is significantly greater than 1 due to the cathodic activity of the CPL leading to higher pH and carbonate concentration (Figures 4b and 4c).

Moreover, by assuming a conductive CPL with a cathodic activity, the corrosion rate obtained is significantly higher (\( V_{corr} = 13.1 \mu m/year \)) than with an insulating CPL (\( V_{corr} = 2.6 \mu m/year \)). Consequently, the concentration of \( Fe^{2+} \) ions is increased as shown in Figure 4d. Under these conditions, it could be concluded that a conductive CPL promotes the stability of the initial deposit.

To understand what controls the saturation level and then the stability of the CPL, the profiles of the saturation level of siderite, of carbonate, \( pH \) and \( Fe^{2+} \) ions are plotted in Figure 5 for an inert and for a conductive CPL at steady state.

The consideration of a conductive CPL induces an increase of the carbonate and \( Fe^{2+} \) concentrations (Figures 5b and 5d) with a \( Fe^{2+} \) concentration being increased in a larger extent compared to that of carbonate. The increase of the saturation level results mainly from the increase of \( Fe^{2+} \) concentration.

Moreover, for a conductive CPL the mechanism given by the literature predicts an acidification at the metal surface due to the depletion of bicarbonate ions leading to a non-protective CPL.25–27 However, in our case, conductive CPL leads systematically to a \( pH \) increase (Figure 7a). This difference can be explained by several factors. Unlike the Cox environment, the medium considered in References 25–27 is acid (\( pH < 6 \)), thus the carbonate concentration is always negligible and the bicarbonate depletion leads to a significant decrease of the \( pH \) under the conductive CPL. In our conditions, water reduction represents 90% of the total cathodic contribution. Thus, the depletion of the bicarbonate resulting from its reduction is negligible in comparison with the production of the hydroxide ions resulting from the water reduction. In a following section additional chemical reactions that could lead to an acidification such as \( FeCO_3(aq) \) or \( FeHCO_3(aq) \) complexes formation will be considered.

**Parametric study.**—Geometrical parameters.—Effect of the thickness of CPL.—A thicker CPL leads to a higher cathodic activity. Consequently, the corrosion rate and the corrosion potential increase as shown in Figure 6a. Note that the cathodic contribution of the CPL is only slightly reduced by the increase of the thickness (Figure 6b) and mainly due to the \( pH \) increase as shown in Figure 7a and the subsequent decrease of the bicarbonate reduction contribution.

The increase of the CPL thickness also leads to the increase of the saturation level of the siderite (Figure 7b) mainly due to the stronger increase of the carbonate concentration in comparison with that of \( Fe^{2+} \) (Figure 7c and Figure 7d). Consequently it is expected that a thicker conductive CPL promotes its stability by the decrease of its porosity.

Effect of the conductive surface area.—It has been assumed that the conductive surface area (\( Sr \)) is lower than the specific surface area (\( Sp \)) of the CPL. In this section a conductive surface representing 1% (as previously), 10% or 25% of the specific surface area of the CPL is considered.

The increase of the conductive surface area implies similar effects as previously with an increase of the corrosion rate resulting from an enhanced cathodic contribution. Therefore, the concentration of the \( Fe^{2+} \) ions increases (Figure 8a). It can be seen that the increase of the siderite saturation level is mainly controlled by the increase of carbonate concentration (Figure 8b) resulting from the \( pH \) increase due to water reduction which is the main cathodic contribution (Figures 8c and 8d).
Effect of the porosity.—Up to now, the porosity was fixed to 0.1 for the CPL. However, in the literature porosity values of 0.001 to 0.5 are observed for siderite CPL.41 In this section, porosity values of 0.2, 10−1 and 10−2 are used.

The decrease of the porosity leads to the increase of the conductive surface area (see Equation 5c) and consequently of the cathodic contribution within the CPL. As previously, the resulting saturation level of siderite is controlled by the increase of the concentration of carbonate (Figures 9a–9b). It is worth noting that these results would be different if there was a parabolic dependence between the porosity and the conductive surface area. With a parabolic dependence the decrease of the porosity leads, above a certain threshold, to the decrease of the cathodic contribution of the CPL (Figure 10d) and the concentration of Fe2+ ions.

Consequently, the corrosion rate increases with the conductivity of the CPL (Figure 10c). Indeed, since the conductivity is low, the electron transfer from the metal to the CPL is limited. Consequently, the cathodic contribution of the CPL (Figure 10d) and the concentration of Fe2+ ions decrease as the conductivity decreases (Figure 11a). And as for the preliminary study, a conductive CPL (σ ≈ 10−5 S.m−1) increases the cathodic contribution and consequently the carbonate ions concentration (Figure 11b) leading to an alkaline medium (Figure 11c). These conditions promote the precipitation of siderite due to high saturation levels (Figure 11d).

These results highlight that a conductive CPL would promote its stability. The higher the conductivity, the higher the saturation levels and consequently the CPL is rather stabilized. It is worth noting that there is a threshold above which the increase in conductivity no longer affects the electrochemical behavior of the CPL.

Electrical properties.—Conductivity of the CPL.—The range of conductivity found in the literature for siderite varies in a large extent between 10−7 and 105 S.m−1.29–31 Such a large range of values results most probably from the presence of secondary phases present in the CPL. As mentioned earlier this secondary phase could be cementite, or magnetite that has a conductivity around 103 S.m−1.30 In the following, conductivities of 10−10, 10−8, 10−5, 1, 10 and 100 S.m−1 are considered.

Figure 10a gives the profiles of the cathodic current densities at steady state for different conductivities of the CPL. There is a significant variation of the cathodic current densities when the conductivity varies from 10−10 to 10−2 S.m−1. For conductivities between 10−2 and 105 S.m−1 the same cathodic current distribution is obtained.

For a CPL conductivity of 10−10 S.m−1 the cathodic current density on the CPL is extremely low. Then the CPL behaves as an insulator. In opposite, the current density obtained for a CPL conductivity ranging from 10−3 to 102 S.m−1 is significant and around several mA.m−2 and it is uniform resulting from uniformity of the Galvani potential ϕϕ - ϕL as shown in Figure 10b.

Consequently, the corrosion rate increases with the conductivity of the CPL (Figure 10c). Indeed, since the conductivity is low, the electron transfer from the metal to the CPL is limited. Consequently, the cathodic contribution of the CPL (Figure 10d) and the concentration of Fe2+ ions decreases as the conductivity decreases (Figure 11a). And as for the preliminary study, a conductive CPL (σ ≈ 10−5 S.m−1) increases the cathodic contribution and consequently the carbonate ions concentration (Figure 11b) leading to an alkaline medium (Figure 11c). These conditions promote the precipitation of siderite due to high saturation levels (Figure 11d).
Metal-CPL specific contact resistance.—The value of the metal-CPL specific contact resistance was set previously to $10^{-2} \, \Omega \cdot m^2$, i.e. to same order of magnitude as that used by Venkatraman. The following values are examined in this section: $\rho_{m-d} = 10^{-2}, 10^{-1}, 10$ and $10^{-2} \, \Omega \cdot m^2$.

As depicted in Figure 12a, the higher $\rho_{m-d}$, the lower the Galvani potential and the cathodic contribution in the CPL. Then, the corrosion rate decreases as the contact resistance increases (Figure 12b). Consequently the siderite saturation level decreases resulting from lower carbonate and $Fe^{2+}$ concentrations, as shown in Figure 13.

This situation (high $\rho_{m-d}$) could be due to a CPL partly detached from the metal surface. These results show that the effect of a conductive CPL is significant when it is in contact with the metal surface.

Complex formation.—It has been demonstrated that accounting for a conductive CPL leads to higher corrosion rates due to an enhanced cathodic contribution through the CPL. The resulting pH increase induced by the cathodic activity is not at all affected by the $Fe^{2+}$ hydrolysis reaction given in Table II. Then, it is relevant to determine whether other complexation reactions could induce an internal acidification as predicted in the literature. Consequently, the stable
Figure 7. a) Profile of the saturation level, b) Profile of the ions carbonate, c) Profile of the pH and d) Profile of Fe$^{2+}$ ions. Parameters: $\varepsilon = 0.1$, $\rho_{m-d} = 0.01 \Omega \cdot m^2$, $\sigma_s = 0.01$ S/m and $Sr = 1\% \times Sp$.

Figure 8. a) Profile of the Fe$^{2+}$ ions, b) Profile of the ions carbonate, c) Profile of the pH and d) Profile of the saturation level. $L = 100 \mu m$, $\varepsilon = 0.1$, $\rho_{m-d} = 0.01 \Omega \cdot m^2$ and $\sigma_s = 0.01$ S/m.
Figure 9. a) profile of the ions carbonate (a), profile of the saturation level (b), evolution of the corrosion rate (c), and profile of the Fe$^{2+}$ ions (d). Parameters: $L = 100 \, \mu m$, $\rho_{m-d} = 0.01 \, \Omega \cdot m^2$, $\sigma_s = 0.01 \, S/m$ and $Sr = 1\% Sp$.

Figure 10. a) profiles of the cathodic current densities, b) profile of the Galvani potential $\phi_s - \phi_L$, c) evolution of the corrosion rate and d) profile of the ratio of the total cathodic current (metal / CPL). Parameters: $L = 100 \, \mu m$, $e = 0.1$, $\rho_{m-d} = 0.01 \, \Omega \cdot m^2$, and $Sr = 1\% Sp$. 

complexes $FeCl_{aq}^{+}$, $FeHCO_{aq}^{+3}$ and $FeCO_{aq}^{3-}$ have been considered. The complexation reactions with their thermodynamic constant are given in Table IX.

Taking into account the complexation reactions greatly affects the $Fe^{2+}$ concentration as shown in Figure 14a whereas the carbonate concentration remains unchanged (Figure 14b). Thus, the decrease of the siderite saturation level (Figure 14c) is only due to the decrease of the $Fe^{2+}$ concentration. It should be mentioned that the same corrosion rate is obtained ($i.e. V_{corr} = 13.1 \mu m/year$) since the electrochemical behavior is not affected by the new complexation reactions.

In fact, the $FeCO_{aq}^{3-}$ complex is the most stable but its concentration is the lowest since the concentration of $CO_2^{3-}$ is lower than those of $HCO_{aq}^{-3}$ and $Cl^{-}$ (Figure 14d).

The complexes $FeCl_{aq}^{+}$ and $FeHCO_{aq}^{+3}$ are formed preferentially and lead to the depletion of $Fe^{2+}$ ions. Finally, these complexation reactions have no influence on the pH distribution through the CPL.
Table IX. Complexation reactions.

| Reaction | Rate | Complexation reaction | $\log \beta$ at 25°C |
|----------|------|-----------------------|----------------------|
| $R_{FeCl^+}$ | $k_{FeCl^+} F_{FeCl^+} a_{Fe^{2+}} a_{Cl^−} - k_{FeCl^+} a_{FeCl^+}$ | $Fe^{2+} + Cl^− \rightleftharpoons FeCl^+$ | $k_{FeCl^+}^{k_{FeCl^+}}$ |
| $R_{FeHCO_3^+}$ | $k_{FeHCO_3^+} F_{FeHCO_3^+} a_{Fe^{2+}} a_{HCO_3^−} - k_{FeHCO_3^+} a_{FeHCO_3^+}$ | $Fe^{2+} + HCO_3^− \rightleftharpoons FeHCO_3^+$ | $k_{FeHCO_3^+}^{k_{FeHCO_3^+}}$ |
| $R_{FeCO_3(aq)}$ | $k_{FeCO_3(aq)} F_{FeCO_3(aq)} a_{Fe^{2+}} a_{CO_3^{2−}} - k_{FeCO_3(aq)} a_{FeCO_3(aq)}$ | $Fe^{2+} + CO_3^{2−} \rightleftharpoons FeCO_3(aq)$ | $k_{FeCO_3(aq)}^{k_{FeCO_3(aq)}}$ |

It must be emphasized that the undersaturation level of siderite is also observed for a non-conductive CPL when these $Fe^{2+}$ complexation reactions are considered.

Conclusions

The objective of this paper is to present a stability study of a conductive CPL when a galvanic coupling between the surface of the metal and the CPL takes place.

The model is based on the porous electrodes theory developed by Newman and is adequate to a mechanistic approach with a limited number of chemical species.

The simulation results showed that considering a conductive CPL leads to an increase of the cathodic contribution and consequently of the carbonate concentration. At the same time, the corrosion rate and the $Fe^{2+}$ ions concentration increase due to the galvanic coupling between the CPL and the surface of the metal.

These conditions lead to high saturation levels of siderite and alkaline pH and then to a stabilization of the CPL. The siderite saturation level is raised if the conductance of the CPL is promoted either by increasing its conductivity, its thickness, the area of the conductive surface or by decreasing the porosity or the specific contact resistance. Furthermore there are thresholds of resistivity and contact resistance above which the CPL behaves mainly as an insulator. Below these thresholds the magnitude of the cathodic activity is uniform over the CPL.

Finally, the effect of mass transport of species was also demonstrated for low porosity values for which the limited release of $Fe^{2+}$ ions leads to high saturation levels.

The internal acidification of the medium underneath the conductive CPL sometimes raised in the literature has not been verified because the medium is buffered by the carbonate, thus the cathodic activity leads to a pH increase within the CPL.

Otherwise, taking into account $Fe^{2+}$ complexation reactions, a $Fe^{2+}$ ions depletion leading to an undersaturated siderite and thus to a destabilized CPL is obtained, but the pH is unchanged.

Work is in progress to modify the numerical model in order to enable the initial deposit to evolve in thickness and porosity, and the motion of the metal-CPL interface, providing a more realistic description of the corrosion rate evolution of the metal.
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Figure 14. a) Profile of the Fe2+ ions, b) Profile of the ions carbonate, c) Profile of the saturation level of the siderite and d) Evolution of the fraction of different complexes present in the system. Parameters: L = 100 μm, ε = 0.1, ρ0-d = 0.01 Ωm², σ0 = 0.01 S/m and Sr = 15% x Sp.

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