Modeling of the propagation of crevice corrosion

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Abstract

Models of crevice corrosion can be divided into two categories: the first one is aimed to define the time necessary to reach a Critical Crevice Solution susceptible to initiate a stable crevice propagation whereas the second one is focused on the chemical composition and potential in the crevice during its steady propagation. In this second category the geometry of the crevice is kept constant which is a very rough approximation since a real crevice never reaches a steady state mainly because of its shape evolution. Such an approach necessitates the determination of the most important input parameters (external solution composition, applied potential, shape of the crevice,..) in the stabilization of a crevice providing a stability criterion is defined, taking into account the occurrence of precipitation or of gas evolution.
The objective of this study was to determine under which conditions of pH and potential a crevice was susceptible to repassivate. For doing this we used commercial code, since existing ones are mostly home-made, keeping in mind that it had to be as a modular as possible. This code was developed using the Chemical Engineering Module of FEMLAB®, which is a MATLAB®-based tool for finite element methods.
In a first part of this study the ability of this software to be used for crevice corrosion on iron will be presented. As function of the environment (bulk composition and applied potential), calculations were performed in order to determine the occurrence of solid precipitation like $FeCl_2$ and $Fe(OH)_2$ or H_2 gas bubbles generation inside the occluded cavity.

Keywords: Crevice corrosion, FEM, steady states

Introduction

Models of crevice corrosion can be divided into two categories: the first one is aimed to define the time necessary to reach a critical crevice solution susceptible to initiate a stable crevice propagation [1,2,3] whereas the second one is focused on the chemical composition and potential in the crevice during its steady propagation [4,5,6]. In this second category the geometry of the crevice is kept constant which is a very rough approximation since a real crevice never reaches a steady state mainly because of their shape evolution. Such an approach necessitates to determine the most important input parameters in the stabilization of a crevice with a given geometry providing a stabilization criteria is defined, e.g. pH, precipitation, gas evolution,…The initial objective of this study was to determine under which conditions of pH and potential a crevice was susceptible to repassivate. For doing this we used commercial code, since existing ones are mostly home-made, keeping in mind that it had to be as a modular as possible. This code was developed using the Chemical Engineering Module of FEMLAB®, which is a MATLAB®-based tool for finite element methods. In a first part of this paper will be presented the ability of this software to be used for crevice corrosion

on iron by comparing our results with previous studies. Then calculations are performed in order to determine in which conditions heterogeneous phases (precipitation, hydrogen generation) is susceptible to appear.

Model Description

Shape and dimension of the crevice

A fixed rectangular shaped crevice is considered, with a width "w" and a depth "l", with l>>w. As generally accounted for in the literature, this crevice is reduced into a one-dimensional problem in order to decrease the time of calculation. The x-axis is oriented along the length of the crevice, x=0 and x=l corresponding respectively to the crevice mouth and tip.

Transport of chemical species

Transport by convection inside the crevice can be neglected since the crevice geometry is fixed. Like most of the authors dealing with simulation of crevice corrosion, transport by diffusion and electromigration is used in our calculation [3-7]. The ionic mobility is proportional to the diffusivity according to the Einstein's relation, and the diffusion coefficient of a component is supposed to be independent of its concentration. The dilute solution approximation is used. Ionic interactions have been taken into account by Walton et al.[4] who showed that dilute solution hypothesis was a good approximation for ionic concentrations below 1 M. Local electroneutrality of the solution is assumed, instead of Poisson's law, meaning that no charge separation is induced by transport. It was checked that calculation performed using electroneutrality and Poisson's law led to the same profiles except in the immediate vicinity of the mouth where the potential drop is the highest.

Homogeneous reactions

According to Sharland [6] a realistic crevice solution must include at least six components that are a supporting electrolyte, e.g. a NaCl solution, one metal cation, hydronium, hydroxide and an hydroxo-metal complex. The four last ions are involved in both chemical reactions :

$$Fe^{2+} + H_2O = H^+ + FeOH^+ \quad (1)$$
$$H_2O = H^+ + OH^- \quad (2)$$

To our knowledge chemical reactions occurring inside the crevice are always considered as elementary and in equilibrium, which has never been experimentally demonstrated. In these conditions the equilibrium constant K_i is equal to the ratio :

$$k_{if} / k_{ib}$$

where k_{if} and k_{ib} are respectively the forward and backward rate constants. Thus accounting for several metal cations and kinds of complexes as sometime reported [5] is not obvious since only equilibrium constants and not rate constants are known. In the numerical treatment it is possible to avoid the use of rate constants in the calculation by combining some transport equation, as proposed in References [5,6]. However this method necessitates a rewriting of a part of the code whenever a reaction is changed or added. Walton [4,7] proposed a general form for the expression of the rate of reaction, allowing a better modularity of his code. In our calculation the values of the rate constants were taken sufficiently high to consider the reactions fast in comparison with the transport processes, but keeping their ratio equal to the equilibrium constant. Then unless specified kinetics constants in the backward direction for

reactions (1) and (2) are respectively $k_{feb}=10^9$ L.mol^{-1}.s^{-1} and $k_{wb}=10^{14}$ L.mol^{-1}.s^{-1}, the kinetics constants in the forward direction being kept as equal to 1, as generally used [3,4,7].

Reactions at the interface

Experimental anodic polarization curve in the bulk electrolyte is generally used in simulations performed on passive metals. Discretizing this curve [7], or fitting it with a polynome [7] has the inconvenient to ignore the evolution of the solution composition, more especially its pH. Moreover, the occurrence of an active passive transition for passive metals in highly aggressive environments such as those encountered in crevices is still subject to debates. As done by others [5,6], we use in this model the Tafel expressions given by Turnbull [9] for iron dissolution and hydronium reduction, i.e. :

$$i_1 = i_{01}\exp[\ F\frac{(V_m-\Phi)}{RT}]$$

$$i_2 = k_{H^+}[H^+]\exp[-0.5F\frac{(V_m-\Phi)}{RT}] \qquad (4)$$

i_1 and i_2 being referred to current densities for iron oxidation and proton reduction respectively, with i_{01} =27.10^{10} A.m^{-2} , k_{H+} = 2.10^{-4} A.mol^{-1}.m. Proton reduction leads to the formation of dissolved hydrogen. We will consider that gaseous hydrogen is formed above a saturation limit of 5.10^{-4} mol.L^{-1}.

Governing equations

Considering the following notation for aqueous species concentrations:
[Cl$^-$]= C_1, [Na$^+$]= C_2, [Fe^{2+}]= C_3, [FeOH$^+$]= C_4, [H$^+$]= C_5 and [OH$^-$]= C_6. The mass conservation equations in the steady state for active walls can be written as :

$$D_1[\nabla^2 C_1 - \frac{F}{RT}\nabla(C_1\nabla\Phi)] = 0 \qquad (5)$$

$$D_2[\nabla^2 C_2 + \frac{F}{RT}\nabla(C_2\nabla\Phi)] = 0 \qquad (6)$$

$$D_3[\nabla^2 C_3 + \frac{2F}{RT}\nabla(C_3\nabla\Phi)] - k_{fef}\ C_3 + k_{feb}C_4C_5 = -\frac{i_1}{Fw} \qquad (7)$$

$$D_4[\nabla^2 C_4 + \frac{F}{RT}\nabla(C_4\nabla\Phi)] + k_{fef}C_3 - k_{feb}C_4C_5 = 0 \qquad (8)$$

$$D_5[\nabla^2 C_5 + \frac{F}{RT}\nabla(C_5\nabla\Phi)] + k_{fef}C_3 - k_{feb}C_4C_5 + k_{wf} - k_{wb}C_5C_6 = \frac{2i_2}{Fw} \qquad (9)$$

$$D_6[\nabla^2 C_6 - \frac{F}{RT}\nabla(C_6\nabla\Phi)] + k_{wf} - k_{wb}C_5C_6 = 0 \qquad (10)$$

If inert walls are considered then the terms in the right hand side of Equations (7) and (9) are null.

If aqueous hydrogen is considered, then a seventh equation is added :

$$D_7\nabla^2 C_7 = \frac{-i_2}{Fw} \qquad (11)$$

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Boundary conditions

As will be seen in our calculations, ignoring the outside solution leads to mathematical instabilities due to steep potential and concentration gradients at the crevice mouth. In the absence of concentration gradients, using Laplace's equation in the bulk solution [4,7] evidenced a significant potential drop in the immediate vicinity outside of the crevice mouth. In the present study the system is limited to the crevice itself, with the tip at x=0 and the mouth at x=l. The boundary condition are the following :

$$\text{for x=0,} \quad \begin{cases} C_2 = C_{20} \\ C_3 = C_{30} \\ C_4 = \dfrac{K_1 C_{30}}{C_{50}} \\ C_5 = C_{50} \\ C_6 = \dfrac{K_2}{C_{50}} \\ C_1 = \sum_{i \neq 1} z_i C_i \\ f(x=0) = 0 \end{cases} \qquad \text{for x=l,} \quad \begin{cases} N_{Fe^{2+}} = \dfrac{i_1}{2F} \\ N_{H^+} = -\dfrac{i_2}{F} \end{cases}$$

In the following, C_{20} is always equal to 10^{-3} mol/l^{-1}.
The list of symbols is given in Table 1.

Results and Discussion

Comparison with existing modeling results

In Figure 1 are shown the concentration profiles in a crevice with active walls, taking into account the same parameters as in Reference [5], i.e. pH=7 and V_m=-0.2 V/ECS at the mouth. For mathematical reasons, the Fe^{2+} concentration at the mouth is weak but not null: $C_{30}=10^{-6}$ mol/L. The concentration profiles are identical to those previously published [5], except a higher pH value (*ca.* 0.5 pH unit) inside the crevice. The origin of this difference can be the result of slightly different values of parameters like equilibrium constant, or to the resolution method since this author did not used the same mathematical formulation for the reaction rate, as explain before.

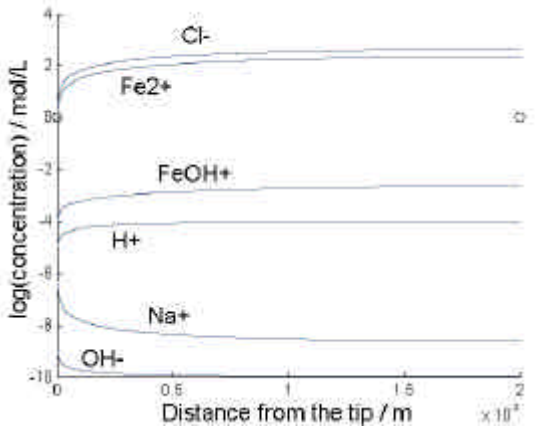

Figure 1: concentration profiles obtained by FEMLAB for conditions described in refs [4,10]

Considering the concentrations of Fe^{2+} and Cl^- inside the crevice, it is obvious that the dilute solution hypothesis cannot hold and that precipitation reaction leading to the formation of solid $FeCl_2$ should be taken into account since its solubility constant is 2.5 at 25°C. This observation is still valid in the case of passive walls where concentrations of Fe^{2+} and Cl^- in the crevice are one order of magnitude lower. Then such a simulation should account for precipitation of solid species like $FeCl_2$ or $Fe(OH)_2$
Considering these precipitates as diffusing entities, i.e. treating these equilibrium like homogeneous reactions as previously reported [5,8] is a too rough approximation, since it ignores the tortuosity increase due to a solid phase formation.

Influence of other existing species in the chemical evolution inside the crevice
Definition of stability domains of solid species like $FeCl_2$ or $Fe(OH)_2$ and gaseous like H_2 have been studied as they are controlling chemical transport inside the crevice and can affect the repassivation process. Such a study allows also to define the limit of validity of the modeling strategy which has been assumed to be only valid in case of homogeneous media.

The results are based on the definition of steady states for a fixed crevice length ($L=2.10^{-3}$ m) and for various crevice width w, as function of external parameters: Cl^- and Fe^{2+} bulk concentrations, pH and applied potential V_m.
Compared to the initial set of equation described in the previous paragraph, the following equilibrium have been added taking into account $FeCl^+$, $Fe(OH)_{2,diss}$ and $H_{2,diss}$:

$Fe^{2+} + Cl^- = FeCl^+$ with $K_{eq.}= [FeCl^+]/[Cl^-][Fe^{2+}]=10^{0.36}$ $L.mol^{-1}$ (from ref [4])

$Fe(OH)^+ + H_2O = Fe(OH)_{2,diss} + H^+$

with $K_{eq.}= [Fe(OH)_{2,diss}][H^+]/[Fe(OH)^+]=10^{-11.1}$ $mol.L^{-1}$ (from ref [10])

The threshold values for precipitation reactions were taken from the literature:

- $FeCl_{2,s} = Fe^{2+} + 2Cl^-$

with $K_s=10^{0.4}= [Fe^{2+}] [Cl^-]^2$ (from ref [9])

- $Fe(OH)_{2,solid} = Fe(OH)_{2,diss}$

with $K_s= [Fe(OH)_{2,diss}]=1,44.10^{-8}$ $mol.L^{-1}$ (from ref [4])

Hydronium reduction was supposed to lead gaseous hydrogen above a solubility threshold according to :

- $H_{2,gas} = H_{2,diss}$

with $K_s= [H_{2,diss}] = 5.10^{-4}$ $mol.L^{-1}$ (from ref [10])

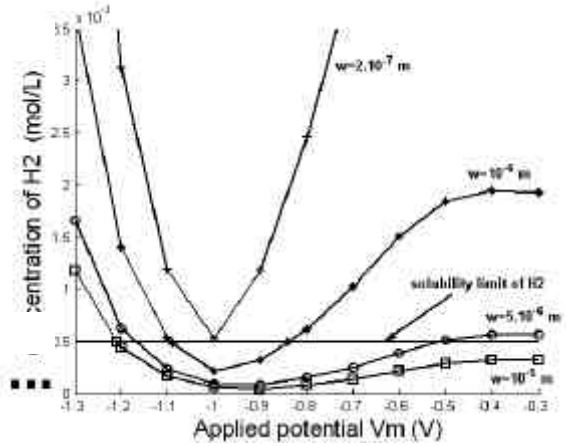

Figure 2: maximum $H_{2,diss}$ concentration as function of the crevice width and the bulk applied potential V_m
$[Fe^{2+}]_{bulk}=10^{-6}$ mol.L^{-1}, $pH_b=7$, $[Cl^-]_{bulk}=10^{-3}$ mol.L^{-1}

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Figure 2 shows a set of results for the generation of $H_{2,gas}$ as function of the crevice width. Different trends can be observed as function of the crevice width:

- $w>5.10^{-6}$ m, H_2,gas generation occurs only for cathodic potentials,
- $w>2.10^{-7}$ m, H_2,gas generation can occur for more anodic potentials,
- $w=2.10^{-7}$ m, H_2,gas generation is independent of all the bulk parameters

If the H_2,gas generation in cathodic domain can be related to the potential control, in the more anodic region the H_2,gas generation can only be related to the hydrolysis of metallic cations which controls the acidification of the electrolyte of the occluded cell.

Following the same strategy, precipitation of solid phases have been revealed as shown in figures 3 and 4. These diagrams clearly show the stability domains of the solid and gaseous species inside the crevice as function of the bulk parameters like the chloride concentration or the applied polarization.

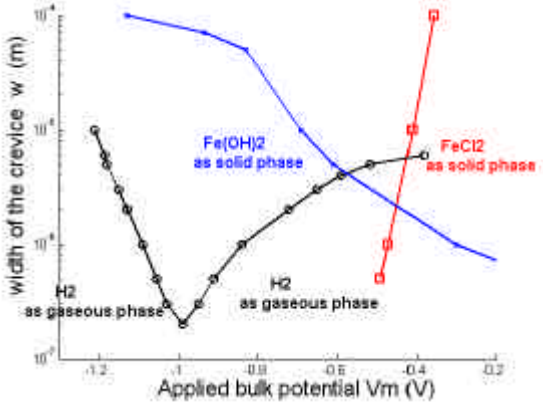

Figure 3: Chemical diagrams as function of the applied bulk potential $[Fe^{2+}]_{bulk} = 10^{-6}$ *mol.L*$^{-1}$, $pH_b=7$, $[Cl^-]_{bulk} = 10^{-3}$ *mol.L*$^{-1}$

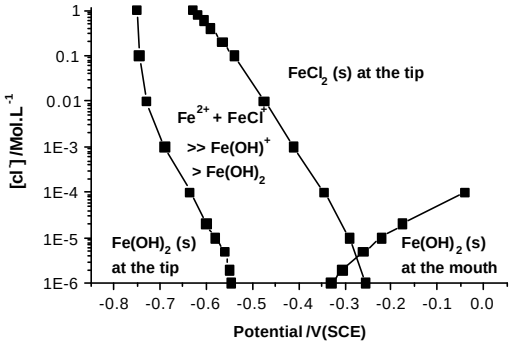

Figure 4: Chemical diagrams as function of the applied bulk potential $[Fe^{2+}]_{bulk} = 10^{-6}$ *mol.L*$^{-1}$, $pH_b=7$, $w=10^{-5}$ *m*

The definition of existence of "homogeneous phases" clearly confirm the preeminence of the controlling parameters: crevice width, bulk imposed potential and bulk chloride concentration.
The other domains of the diagrams related to heterogeneous media (precipitation, gas generation) clearly illustrate the limits of the proposed modeling strategy and the necessity to introduce precipitation or gaseous evolution in the set of equations governing the reactions inside the crevice.

Application of the model: conditions for crevice propagation

The main objective of this study is to validate the existence of critical criterion regarding the propagation arrest which would depend on bulk parameters (typically the repassivation potential) or on occluded cell characteristics (typically pH of repassivation).
On the basis of the diagrams shown in figures 2, 3 or 4, the study of crevice propagation or arrest must be performed for bulk conditions leading to an homogenous medium.

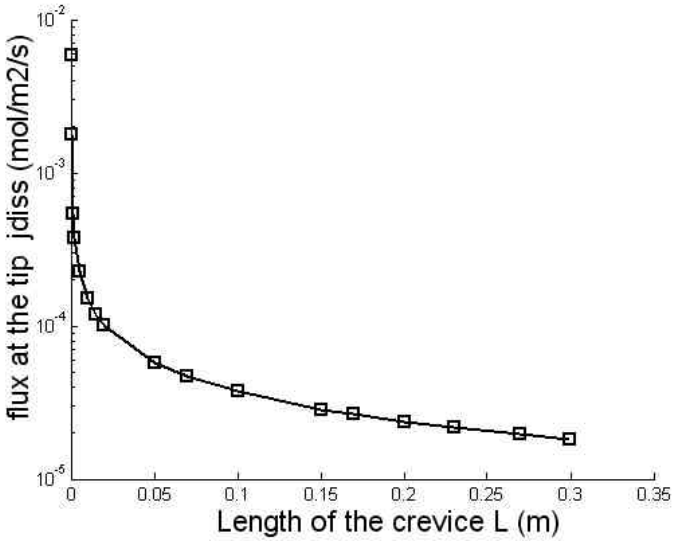

Figure. 5 - Dissolution flux at the crevice tip as function of the crevice length $[Fe^{2+}]_{bulk} = 10^{-6}\ mol.L^{-1}$, $[Cl^-]_{bulk} = 10^{-3}$, $pH_b = 7$, $V_m = -0.4V$

The propagation steps of the crevice can be described as successive steady states. For example the current density (of the flux of dissolution) at the crevice tip can be calculated as function of the length of the crevice.
It can be seen that the critical controlling parameters describing the chemical and electrochemical behavior of the occluded cell can be described by this approach and for example the current density at the tip of the crevice can be calculated as function of the length of the crevice. As shown in Figure 5, the observed trend confirms the decrease of the propagation rate as function of the crevice growth.

Conclusion

In this study it was demonstrated that a code developed using the Chemical Engineering Module of FEMLAB® can be used to simulate the crevice propagation in steady states conditions.
The first results obtained by the simulation allows to determine that crevice width, imposed potential and bulk chloride concentration are the controlling parameters which affects the chemistry in an occluded cell and consequently the crevice propagation. These results have been obtained by introducing the equilibrium concerning hydrogen generation and the precipitation of solid iron hydroxide and ferrous chloride. Physico-chemical diagrams describing the existence of heterogeneous or homogeneous phases inside the crevice have been introduced.
Assuming crevice propagation steps as successive steady states, a trend for crevice arrest can be evaluated.
Work is in progress to study the role of other metallic cations (chromium and nickel) on the chemical evolution of the crevice.

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TABLE 1

SYMBOLS CAPTION

C_i (i=1..7)	Concentrations inside the crevice	$mol.L^{-1}$
C_{i0} (i=1..7)	Concentrations at the crevice mouth	$mol.L^{-1}$
D_i (i=1..4,7)	Diffusion coefficient	10^{-9} m^2.s-1
D_5	Diffusion coefficient of H^+	9,3.10^{-9} m^2.s-1s
D_6	Diffusion coefficient of OH^-	5,3.10^{-9} m^2.s-1
F	Faraday's constant	96483 $C.mol^{1}$
i_{01}	Exchange current density	27.10^{10} $A.m^{-2}$
K_i	Equilibrium constant for reaction i	
k_{fef}	Kinetic constant (forward reaction (1))	1 s^{-1}
k_{feb}	Kinetic constant (backward reaction (1))	$10^{9,5}$ $L.mol^{-1}.s^{-1}$
k_{wf}	Kinetic constant (forward reaction (2))	1 $L.mol^{-1}.s^{-1}$
k_{wb}	Kinetic constant (backward reaction (2))	10^{14} $L.mol^{-2}.s^{-1}$
k_{H+}	Exchange current density	2.10^{-4} $A.L.mol^{-1}.m^{-2}$
l	Crevice depth	m
N_i	Flux of species i	$mol.s^{-1}.m^{-2}$
pH_b	pH in the bulk solution	
R	Gas constant	8,31 $J.mol^{-1}.K^{-1}$
T	Temperature	298 K
w	Crevice width	m
Φ	Electrostatic potential	V
V_m	External potential of the metal	V

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