

## DISTRIBUTION OF ELECTROCHEMICAL REACTION COMPONENTS IN CREVICE CORROSION CELL

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**Summary** In this paper numerical model of the crevice corrosion is developed. The model considers electrochemical reactions for the iron on the metal electrolyte boundary and chemical reactions which take place in the crevice electrolyte. Mass transfer of ionic species is described by Nernst-Planck equation and is solved with the finite element method in two dimensions. On the problem boundary adequate boundary conditions are defined. Distribution of all chemical species, potential and current density in the crevice and on the crevice walls are computed. In mass balance for particular chemical species the speed of the chemical reactions is taken into account. At the end some illustrative example is given.

### 1. INTRODUCTION

Numerical models of crevice corrosion can help to improve the understanding and protection of the corrosion process. Such models can be used for comparisons purposes between different corrosion theories and between theories and results of experiments. In some cases it is difficult to measure all corrosion parameters on the corroding surface and in the electrolyte near corroding places so the mathematical models can help to understand measurement results. Such numerical approach is especially useful for the localized corrosion, such as crevice or pitting corrosion, where problem is described by high number of nonlinear partial differential equations mutually coupled by nonlinear boundary conditions and nonlinear rates of production or depletion ionic species in electrolyte. In [1] authors describe simplified method for estimating corrosion growth rates using simplified one dimensional model and solve it analytically using quasi-potential variable. They consider all chemical reactions only in equilibrium state. In [2] authors use finite element method for simulation of the time propagation of crevice corrosion. They develop problem equations in two dimensions but partial differential equations describing electric potential distribution consider in very simplified form. Moreover these equations are solved also in one dimension though authors suggest that two dimensional grid may be used for numerical analysis. In [3] author developed mathematical model of mass transport and chemical reactions in crevice in one dimension for acetate and sulfuric acid electrolyte. Author obtained good agreement between theoretical prediction and the experimental results but as in the previous publications only one dimensional model and simplified Laplace equation for electric potential is used. Authors of other publications [4,5,6] on the crevice corrosion process follow this way of modeling.

In this paper authors developed full model of crevice corrosion process described by set nonlinear partial differential equations and full form of Laplace equation for electric potential variable. This set of equations is solved in two dimensions. Distribution of molar concen-

tration and fluxes of ionic species and current density in the crevice is determined.

### 2. CONCEPTUAL MODEL OF CREVICE CORROSION

The crevice corrosion can cause dangerous situations in practical applications. Its size can vary in wide range of dimensions from microcrevice ( $\sim 1 - 100 \mu\text{m}$ ), that may damage painting coating, thin membranes, etc., and large corrosion cavities ( $\sim 1 - 10 \text{ mm}$ ) leading to corrosion cracks and perforation of, for example, container walls. In fig. 1 simplified model of crevice is presented.

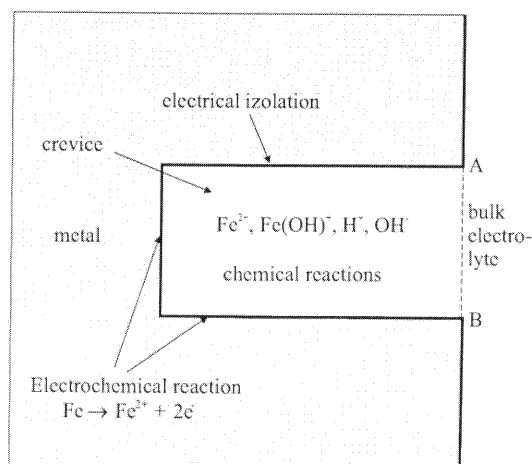


Fig.1. Simplified model of crevice corrosion.

In the piece of metal, in our case iron, the rectangular cavity is drawn. It is assumed that upper wall is isolated so the corrosion take place on the left and bottom sides. From the right side the crevice contacts with bulk electrolyte which volume is considerably greater than volume of the crevice. This allows us to assume that all chemical species in this bulk electrolyte and thus on the boundary A-B do not change with time and are constant.

It is assumed that cavity contains four different ionic species,  $S_k$ :

$$S_1: Fe^{2+}, S_2: Fe(OH)^+, S_3: H^+, S_4: OH^- \quad (1)$$

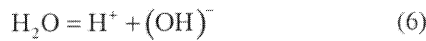
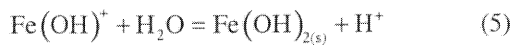
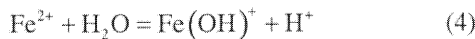
The concentration of individual species are named as follows:

$$C_1 = [Fe^{2+}], C_2 = [Fe(OH)^+], C_3 = [H^+], C_4 = [OH^-] \quad (2)$$

It is assumed that single electrochemical reaction at anode takes place:



and additionally three homogeneous chemical reactions occur in the crevice electrolyte:



where  $Fe(OH)_{2(s)}$  represents precipitated hydrolysis product,  $Fe(OH)^+$  metal hydrolysis product,  $OH^-$  hydroxyl ions and  $H^+$  hydrogen ions. Electrochemical reaction (3) take place on the left and bottom boundary and chemical reaction (4) – (6) in the crevice electrolyte. It is further assumed that in the crevice electrolyte  $Na^+$  and  $Cl^-$  are present but they do not react with other species.

### III. GOVERNING EQUATIONS

The molar fluxes of individual species in electrolyte can be defined by most fundamental Nernst-Planck equation in general form:

$$\mathbf{N}_i = -z_i \frac{F}{RT} D_i C_i \nabla \varphi - D_i \nabla C_i \quad (7)$$

where  $i = 1, 2, 3, 4$ . The first term on the right-hand side of the above equation represents migration and the second term represents diffusion. The total current density flowing in electrolyte is given by:

$$\mathbf{J} = F \sum_{i=1}^n z_i \mathbf{N}_i \quad (8)$$

The next assumption assumes that electrolyte at every point is neutral:

$$\sum_{i=1}^n z_i C_i = 0 \quad (9)$$

It is well known that current density field is conservative, so [7, 8]

$$\nabla \cdot \mathbf{J} = 0 \quad (10)$$

at every point within the electrolyte. Mass conservation law in terms of molar concentrations can be written as:

$$\frac{\partial C_i}{\partial t} + \nabla \cdot \mathbf{N}_i = R_i \quad (11)$$

where  $R_i$  is the rate of generation of species  $i$ . One can multiply every above equation by  $z_i$  and after summation we get:

$$\frac{\partial}{\partial t} \sum_{i=1}^n z_i C_i + \nabla \cdot \sum_{i=1}^n z_i \mathbf{N}_i = \sum_{i=1}^n z_i R_i \quad (12)$$

Introducing (9) and (10) into (12) and after some manipulations one gets:

$$\sum_{i=1}^n z_i R_i = 0 \quad (13)$$

From equations (7) and (8) we have:

$$\mathbf{J} = -\sum_{i=1}^n z_i^2 \frac{F^2}{RT} D_i C_i \nabla \varphi - \sum_{i=1}^n F z_i D_i \nabla C_i \quad (14)$$

or after rearrangement of terms:

$$\left( \sum_{i=1}^n z_i^2 \frac{F^2}{RT} D_i C_i \right) \nabla \varphi = -\mathbf{J} - \sum_{i=1}^n F z_i D_i \nabla C_i \quad (15)$$

Introducing ionic conductivity  $\kappa$  as:

$$\kappa = \sum_{i=1}^n z_i^2 \frac{F^2}{RT} D_i C_i \quad (16)$$

we have

$$\kappa \nabla \varphi = -\mathbf{J} - \sum_{i=1}^n F z_i D_i \nabla C_i \quad (17)$$

or

$$\nabla \varphi = -\frac{1}{\kappa} \left( \mathbf{J} + F \sum_{i=1}^n z_i D_i \nabla C_i \right) \quad (18)$$

The mass balance equation (11) in expanded form after introducing (7) can be written as:

$$\frac{\partial C_i}{\partial t} - z_i \frac{F}{RT} D_i (\nabla C_i \cdot \nabla \varphi + C_i \cdot \nabla^2 \varphi) - D_i \nabla^2 C_i = R_i \quad (19)$$

It is enough to solve only  $n - 1$  equations because from electroneutrality one can compute the last  $n^{\text{th}}$  ionic concentration. In the steady state one can assume that  $\partial C_i / \partial t = 0$  and thus

$$\nabla^2 C_i + z_i \frac{F}{RT} (\nabla C_i \cdot \nabla \varphi + C_i \cdot \nabla^2 \varphi) = -\frac{1}{D_i} R_i \quad (20)$$

Let us now to take gradient of both sides of equation (15):

$$\nabla \cdot \left[ \left( \sum_{i=1}^n z_i^2 \frac{F^2}{RT} D_i C_i \right) \nabla \varphi \right] = -\nabla \cdot \mathbf{J} - \sum_{i=1}^n F z_i D_i \nabla^2 C_i \quad (21)$$

After some manipulations this equations has the form:

$$\sum_{i=1}^n z_i^2 \frac{F^2}{RT} D_i \nabla C_i \cdot \nabla \varphi + \left( \sum_{i=1}^n z_i^2 \frac{F^2}{RT} D_i C_i \right) \nabla^2 \varphi = -\sum_{i=1}^n F z_i D_i \nabla^2 C_i \quad (22)$$

Utilizing (16) we get:

$$\nabla^2 \varphi = -\frac{1}{K} \left( \sum_{i=1}^n z_i^2 \frac{F^2}{RT} D_i \nabla C_i \right) \cdot \nabla \varphi - \frac{F}{K} \sum_{i=1}^n z_i D_i \nabla^2 C_i \quad (23)$$

Let us eliminate  $\nabla^2 C_i$  from the above equation:

$$\nabla^2 \varphi = -\frac{1}{K} \left( \sum_{i=1}^n z_i^2 \frac{F^2}{RT} D_i \nabla C_i \right) \cdot \nabla \varphi - \frac{1}{K} \sum_{i=1}^n \left( -z_i^2 \frac{F^2}{RT} D_i (\nabla C_i \cdot \nabla \varphi + C_i \cdot \nabla^2 \varphi) - F z_i R_i \right) \quad (24)$$

or after arrangement of terms

$$\nabla^2 \varphi = 0 + \frac{1}{K} \kappa \nabla^2 \varphi + \frac{1}{K} F 0 \quad (25)$$

This means that equations (20) and equation for potential (24) are linearly dependent. Thus the set of  $n-1$  equations:

$$\nabla^2 C_i + z_i \frac{F}{RT} (\nabla C_i \cdot \nabla \varphi + C_i \cdot \nabla^2 \varphi) = -\frac{1}{D_i} R_i \quad (26)$$

and equation

$$\nabla^2 \varphi = -\frac{1}{K} \left( \sum_{i=1}^n z_i^2 \frac{F^2}{RT} D_i \nabla C_i \right) \cdot \nabla \varphi - \frac{F}{K} \sum_{i=1}^n z_i D_i \nabla^2 C_i \quad (27)$$

together with condition:

$$C_n = -\frac{1}{z_n} \sum_{i=1}^{n-1} z_i C_i \quad (28)$$

forms a set of  $n$  equations in  $n$  different  $C_1 \dots C_{n-1}, \varphi$  variables.

In our case equations (27) and (28) have following form:

$$\begin{aligned} \nabla^2 \varphi = & -\frac{1}{K} \left( \sum_{i=1}^3 z_i^2 \frac{F^2}{RT} D_i \nabla C_i \right) \cdot \nabla \varphi 0 - \\ & -\frac{1}{K} z_4^2 \frac{F^2}{RT} D_4 \nabla C_4 \cdot \nabla \varphi \quad (29) \\ & -\frac{F}{K} \sum_{i=1}^3 z_i D_i \nabla^2 C_i - \frac{F}{K} z_4 D_4 \nabla^2 C_4 \\ C_4 = & -\frac{1}{z_4} \sum_{i=1}^3 z_i C_i \quad (30) \end{aligned}$$

#### 4. BOUNDARY CONDITIONS

On the surface where the electrochemical reactions take place following boundary conditions are fulfilled:

$$\frac{\partial C_1}{\partial n} = \left( \frac{1}{2F} + z_1 D_1 C_1 \frac{F}{RT} \right) J_n \quad (31)$$

where  $J_n$  is given by Butler-Volmer equation:

$$J_n = i_0 \left[ \exp\left(\frac{-E_{0a} - V}{\beta_a}\right) - \exp\left(\frac{-E_{0a} - V}{\beta_a}\right) \right] \quad (32)$$

and for electric potential:

$$\frac{\partial \varphi}{\partial n} = -J_n \quad (33)$$

On the crevice and bulk electrolyte boundary ionic species have following concentrations:  $C_1 = 1e-10$ ,  $C_2 = 1e-9$ ,  $C_3 = 1e-14$ ,  $C_4 = 1e-6$ , all dimensions in  $[\text{mol}/\text{cm}^3]$ .

#### 5. AN ILLUSTRATIVE EXAMPLE

Geometrical dimensions of the analyzed problem are given in fig. 2. Following physical parameters are used:  $F = 96485$  [C/mol],  $T = 300$  [K],  $R = 8.31451$  [J/mol/K],  $D_1 = 7.2e-6$  [ $\text{cm}^2/\text{s}$ ],  $D_2 = 1e-5$  [ $\text{cm}^2/\text{s}$ ],  $D_3 = 9.3e-5$  [ $\text{cm}^2/\text{s}$ ],  $D_4 = 5.3e-5$  [ $\text{cm}^2/\text{s}$ ],  $K_1 = 1e-9.8$  [mol/l]. Chemical equilibrium reaction constants:  $K_2 = 1e-4.9$  [mol/l],  $K_w = 1e-13.98$  [(mol/l) $^2$ ].

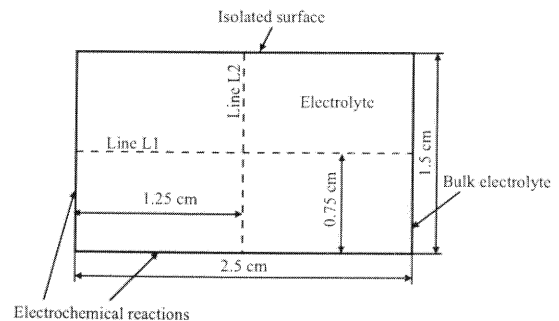


Fig.2. Geometrical dimensions of the crevice cell.

In the fig. 3 molar concentration of the iron ions in function of  $x$  coordinate is plotted. We can see that for  $x = 0$  concentration has greatest value and decreases to the concentration which is in bulk electrolyte. It is the result of diffusion and migration process of iron ions. In the fig. 4. we can see distribution of the electric potential in the crevice electrolyte. It is influence by electrochemical

reaction which on the corroding sites takes place and by electrolyte conductivity. Fig. 5 shows distribution of the current density along the crevice length. The greatest value of the current density is at the mouth of the crevice. It is caused by the fact that is generated along the whole bottom side of the crevice. In the fig. 6 flux of the molar concentration  $N_1$  is shown. Part of the dissolved ions reacts to produce  $Fe(OH)_{2(s)}$  and another part flow out of the crevice to the bulk electrolyte.

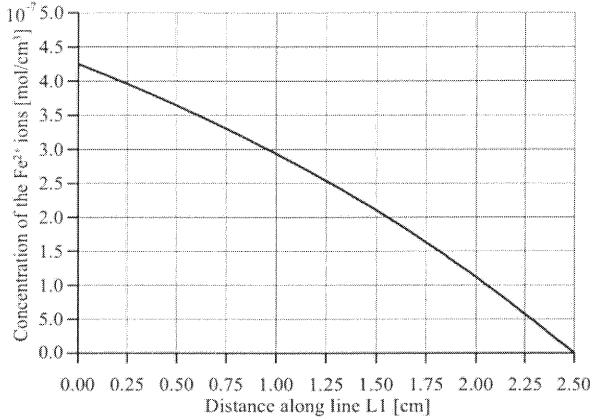


Fig.3. Concentration of the iron ionic species in crevice.

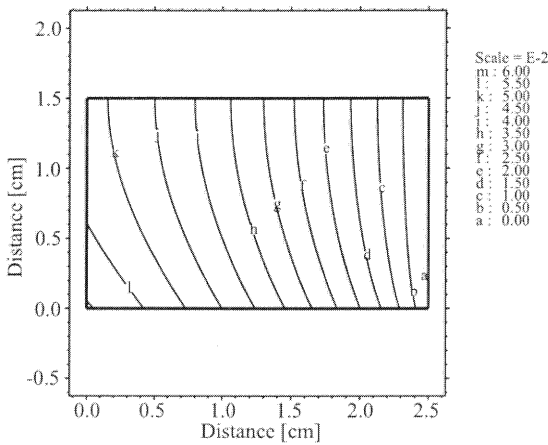


Fig.4. Plot of the electric potential in the crevice.

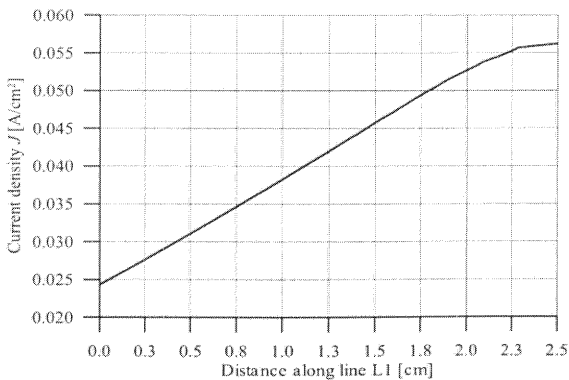


Fig.5. Plot of the current density along the L1 line.

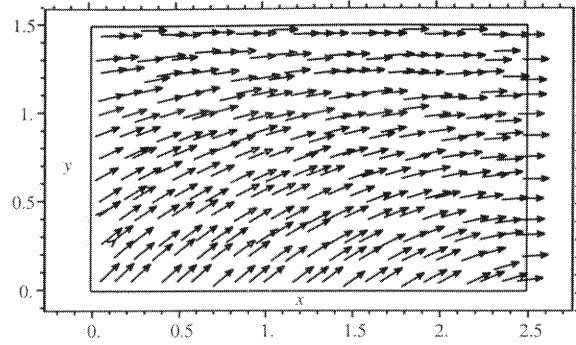


Fig.6. Flux of the molar concentration of iron ions.

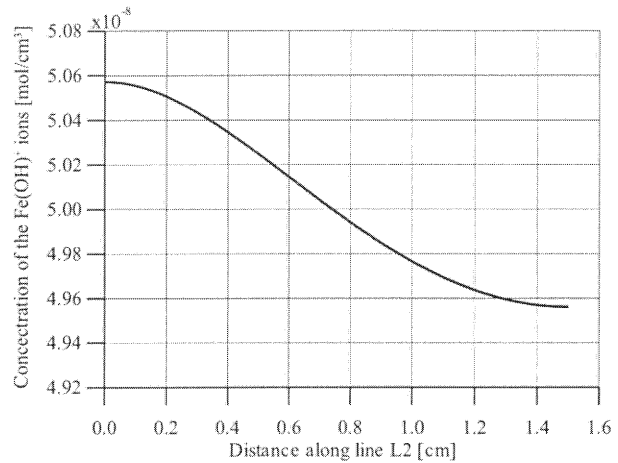


Fig.7. Plot of the molar concentration of the  $Fe(OH)^+$  ions along the L2 line.

### 6. CONCLUSIONS

The numerical simulation presented above shows that knowledge of the iron ion flux on the corrosion part of the boundary allows us to predict the rates of cavity propagation in time. In our article we consider only the case taken from the literature [1] where single electrochemical reaction of the iron within the crevice takes place. However it is clear that the method can be extended where multiple electrochemical reactions occur at the corroding surface [9].

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