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**Development of a time dependant numerical model for the
quantification of AC corrosion phenomena**

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Introduction

In recent years Büchler et al. [1-2] have developed an AC corrosion model that is able to explain why corrosion not only occurs for alternative current signals that have an anodic or nearly zero DC component, but also for alternative current signals where the DC component is cathodic. Depending on the magnitude of the DC component and ratio to the AC current density component, the corrosion rate might rise to values in the order of 0.1 to 70.0 mm/year.

The occurrence of significant corrosion rates for signals with cathodic DC current density components is attributed to the repetitive cathodic breakdown and anodic reformation of a compact oxide barrier layer into a porous rust layer. This is illustrated in figure 1 [2].

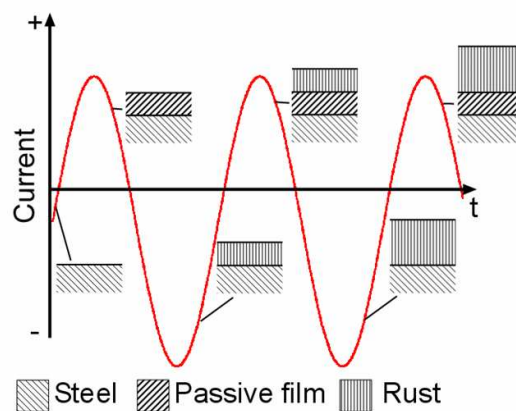


Figure 1: repetitive cathodic breakdown and anodic reformation of a compact oxide barrier layer

The presence of both the compact barrier layer and the porous rust layer has been proven by means of light reflectance techniques and galvanostatic reduction experiments [1].

The basic building blocks of the proposed AC corrosion model are [1]:

- compact barrier oxide layer with high field model voltage drop¹;
- porous oxide/ hydroxide rust layer exhibiting a charge capacitive effect due to the reversible conversion of Fe (II) into Fe (III) and vice versa;
- reduction of the compact oxide layer into a rust layer for sufficiently negative electrode potential values;
- regeneration of the compact oxide layer for sufficiently positive electrode potential values (through oxidation of the bare metal);
- occurrence of hydrogen and oxygen evolution reactions for respectively sufficiently negative and positive electrode potentials;
- decrease of the spread resistance around a defect due to the accumulation of electrochemically produced hydroxide ions in the vicinity of the defect.

¹ where it is assumed that the ohmic drop over the porous oxide rust layer is not significant.

Although a number of aspects of this model have been quantified through experiments and theoretical considerations [1] (e.g. the thickness of the compact barrier layers, charge capacity of the rust layer) from a mathematical and physicochemical point of view this model is not complete; i.e. does not allow for a coherent set of mathematical conservation equations.

In order to create a mathematically sound model the following features are added:

- identification of the species that compose the compact barrier layer and porous oxide rust layer;
- introduction of a variable surface fraction $\theta = f(t)$ for describing a compact rust layer that only partially covers the substrate surface;
- multi-ion transport model for describing the decrease of the spread resistance around the defect and the diffusion of produced oxygen and hydrogen towards the bulk of the soil;
- possibility for the produced oxygen and hydrogen (in dissolved condition) to be reduced (respectively) oxidised at the electrode (this can be regarded as an additional charge capacitive system).

Based upon references [1, 4] the compact oxide layer is assigned to consist of magnetite (Fe_3O_4) and the rust layer is a mixture of maghemite (Fe_2O_3) and iron (II) hydroxide $\text{Fe}(\text{OH})_2$.

Mathematical model formulation

A schematic overview of the different phases and domains to consider in the model is presented in figure 2.

The AC corrosion model requires the definition of a potential value at the interface between the different domains:

- metal potential V_1 ;
- outside barrier layer potential V_2 ;
- soil potential at the rust / soil interface U
- far field soil potential U_{ff} .

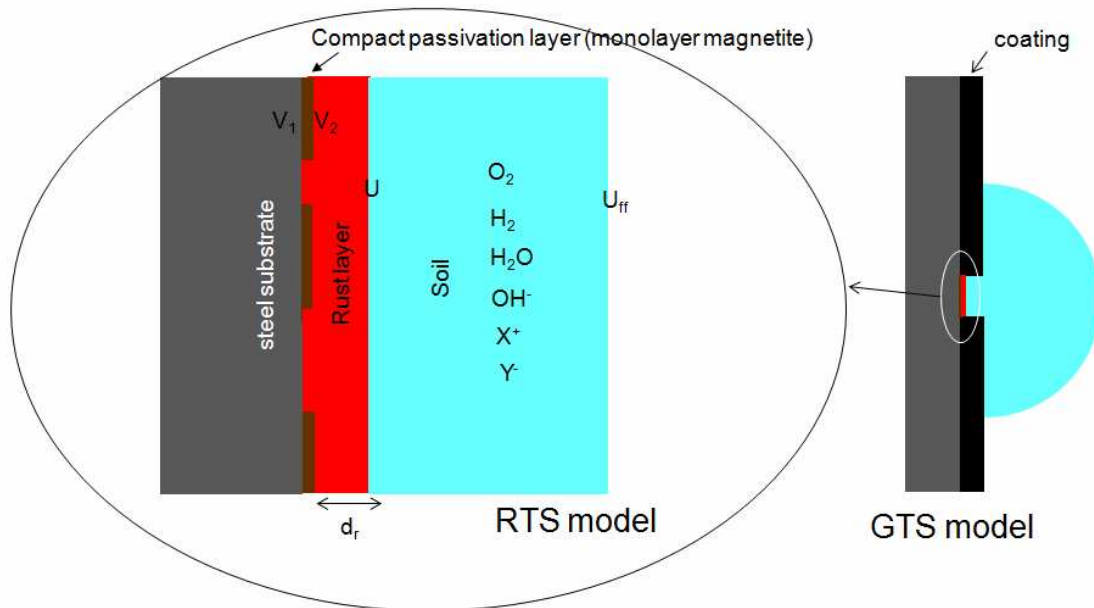


Figure 2: schematic representation of AC corrosion model

Electrode reactions

The electrode reactions can take place both on the bare steel substrate and on the compact oxide layer. The driving force for the reactions on the bare steel surface (V_1-U) is bigger than on the compact oxide layer (V_2-U), due to the potential drop (V_1-V_2) over the oxide layer. Further down in the report, the reaction current densities on the bare steel substrate will be denoted as j_i^* , while j_i^0 is used to describe the current densities on the compact oxide layer.

Table 1 provides an overview of all relevant electrode reactions including their stoichiometry. The reaction current density kinetics are listed in table 2. The driving force η is equal to (V_1-U) on bare steel surface and equal to (V_2-U) on the compact oxide layer. The concentrations indicated with square [] brackets represent soil species concentrations at the rust layer interface. The concentration of the maghemite and iron (II) hydroxide species in the rust layer are indicated with round brackets ().

Reaction	Name	Stoichiometry
1	H ₂ evolution / re-oxidation	$\text{H}_2\text{O} + 2 \text{e}^- = \text{H}_2 + 2 \text{OH}^-$
2	O ₂ reduction / formation	$2 \text{H}_2\text{O} + \text{O}_2 + 4 \text{e}^- = 4 \text{OH}^-$
3	ferro – ferri conversion	$3 \text{H}_2\text{O} + \text{Fe}_2\text{O}_3 + 2 \text{e}^- = 2 \text{OH}^- + 2 \text{Fe}(\text{OH})_2$
4	magnetite oxidation to maghemite	$\text{H}_2\text{O} + 3 \text{Fe}_2\text{O}_3 + 2 \text{e}^- = 2 \text{OH}^- + 2 \text{Fe}_3\text{O}_4$
5	magnetite reduction to iron hydroxide	$4 \text{H}_2\text{O} + \text{Fe}_3\text{O}_4 + 2 \text{e}^- = 2 \text{OH}^- + 3 \text{Fe}(\text{OH})_2$
6	iron oxidation	$4 \text{H}_2\text{O} + \text{Fe}_3\text{O}_4 + 8 \text{e}^- = 8 \text{OH}^- + 3 \text{Fe}$

Table 1: electrode reactions - stoichiometry

Reaction	Name	Bare steel	Oxide
1	$j_1 = k_{a1} [\text{OH}^-] [\text{H}_2] \exp(\alpha_1 2F\eta/RT) - k_{c1} [\text{H}_2\text{O}] \exp(-\beta_1 2F\eta/RT)$	j^*_1	j^o_1
2	$j_2 = k_{a2} [\text{OH}^-] \exp(\alpha_2 4F\eta/RT) - k_{c2} [\text{H}_2\text{O}] [\text{O}_2] \exp(-\beta_2 4F\eta/RT)$	j^*_2	j^o_2
3	$j_3 = k_{a3} [\text{OH}^-] (\text{Fe}(\text{OH})_2) \exp(\alpha_3 2F\eta/RT) - k_{c3} [\text{H}_2\text{O}] (\text{Fe}_2\text{O}_3) \exp(-\beta_3 2F\eta/RT)$	j^*_3	j^o_3
4	$j_4 = k_{a4} [\text{OH}^-] \exp(\alpha_4 2F\eta/RT) - k_{c4} [\text{H}_2\text{O}] (\text{Fe}_2\text{O}_3) \exp(-\beta_4 2F\eta/RT)$	N / A	$j^o_4 > 0$
5	$j_5 = k_{a5} [\text{OH}^-] (\text{Fe}(\text{OH})_2) \exp(\alpha_5 2F\eta/RT) - k_{c5} [\text{H}_2\text{O}] \exp(-\beta_5 2F\eta/RT)$	N / A	$j^o_5 < 0$
6	$j_6 = k_{a6} [\text{OH}^-] (\text{Fe}(\text{OH})_2) \exp(\alpha_6 2F\eta/RT) - k_{c5} [\text{H}_2\text{O}] \exp(-\beta_6 2F\eta/RT)$	$j^*_6 > 0$	N / A

Table 2: electrode reactions – reaction kinetics

The local conservation equation for iron in the rust layer is expressed as:

$$2 (\text{Fe}_2\text{O}_3) + (\text{Fe}(\text{OH})_2) = \gamma_{\max} = 5.0\text{E}+5 \text{ mol/m}^3 \quad (1)$$

For each moment in time the total (microscopically uniformised) current density is written as:

$$j(t) = \theta (j^o_1 + j^o_2 + j^o_3 + j^o_4 + j^o_5) + (1 - \theta) (j^*_1 + j^*_2 + j^*_3 + j^*_6) \quad (2)$$

For a given value of the spread resistance R (depending on size and shape of the defect) the ohmic drop around the defect can be written as:

$$R A j(t) = U(t) - U_{\text{ff}}(t) \quad (3)$$

The voltage drop over the compact oxide barrier layer is expressed by means of a high field model:

$$j^o(t) = k_o \exp(-W/RT) \exp(\beta(V_1 - V_2)/d_c) - k_o \exp(-W/RT) \exp(-(1-\beta)(V_1 - V_2)/d_c) \quad (4)$$

with: W: activation energy = 2.3E-9 J/mol
 k_o : kinetic pre-exponential factor = 6.8E-8 A/m²
 β : transfer coefficient = 5.0E-8 m/V
 d_c : barrier oxide layer thickness = 1.0E-9 m (monolayer)
R: universal gas constant = 8.31 J/mol K

In equation (4) it is assumed that the barrier layer does not grow beyond a monolayer that covers the entire electrode surface. Hence the barrier layer is completely described by a constant thickness d_c and its surface coverage fraction $\theta(t)$.

For a given metal potential V_1 and an imposed far field excitation signal $U_{\text{ff}}(t)$, equations (2), (3) and (4) allow at any moment in time to solve for the potential values V_2 and U , and the total current density $j(t)$.

For a given time step Δt the surface coverage fraction $\theta(t)$ will decrease due to the oxidation or reduction of the magnetite (reactions 4 and 5), and increase due to the oxidation of bare metal (reaction 6). This is mathematically expressed as:

$$\Gamma_{\max} \Delta\theta = (-\theta j^o_4 + 0.5 \theta j^o_5 + 0.125 (1-\theta) j^*_6) \Delta t / F \quad (5)$$

with $\Gamma_{\max} = 2.0\text{E-}6 \text{ mol/m}^2$ (this number is based on typical lattice dimensions of magnetite).

In a similar manner, the thickness of the rust layer will increase due to oxidation or reduction of the magnetite (reactions 4 and 5):

$$\Delta d_{r1} = + \theta 1.5 j^o_4 M_1 \Delta t / \rho F \quad (6)$$

$$\Delta d_{r2} = - \theta 1.5 j^o_5 M_2 \Delta t / \rho F \quad (7)$$

with: M_1 : molecular weight $\text{Fe}_2\text{O}_3 = 160 \text{ g/mol}$
 M_2 : molecular weight $\text{Fe}(\text{OH})_2 = 90 \text{ g/mol}$
 ρ : specific density rust layer $= 3.4\text{E+}6 \text{ m}^3$

The concentration of Fe_2O_3 and $\text{Fe}(\text{OH})_2$ in the initial thickness of the rust layer changes due to the conversion reaction 4, while eq. (1) is always respected:

$$d_r (\text{Fe}_2\text{O}_3)^{n+1/2} = +0.5 (\theta j^o_3 + (1-\theta) j^*_3) \Delta t / F \quad (8)$$

$$d_r (\text{Fe}(\text{OH})_2)^{n+1/2} = -1.0 (\theta j^o_3 + (1-\theta) j^*_3) \Delta t / F \quad (9)$$

The averaged concentration of maghemite and iron (II) hydroxide in the rust layer with increased thickness $d_r + \Delta d_{r1} + \Delta d_{r2}$ at time step $n+1$ is then obtained by averaging the concentrations over the entire rust layer thickness, again obeying eq. (1):

$$2 (\text{Fe}_2\text{O}_3)^{n+1} = +(2 d_r (\text{Fe}_2\text{O}_3)^{n+1/2} + \Delta d_{r1} \gamma_{\max}) / (d_r + \Delta d_{r1} + \Delta d_{r2}) \quad (10)$$

$$(\text{Fe}(\text{OH})_2)^{n+1} = +(d_r (\text{Fe}(\text{OH})_2)^{n+1/2} + \Delta d_{r2} \gamma_{\max}) / (d_r + \Delta d_{r1} + \Delta d_{r2}) \quad (11)$$

The corrosion rate of the steel at any point in time can be easily obtained from Faraday's law being applied to reaction 6:

$$\Delta d = - 3/8 (1-\theta) j^*_6 M \Delta t / \rho F \quad (12)$$

with: M : atomic weight $\text{Fe} = 55.8 \text{ g/mol}$
 ρ : specific density steel $= 8.0\text{E+}6 \text{ m}^3$

Species transport in the soil

From table 2 it follows that the kinetics of most reactions depends on the concentration of species in the soil, adjacent to the steel substrate. For example the kinetics of reaction 2 depends for its cathodic branch upon the oxygen concentration in the soil. The oxygen is either produced previously by reaction 2 proceeding in anodic direction or transported from the bulk of the soil. Basically 3 species are being produced or consumed by the electrode reactions: oxygen, hydrogen and hydroxide ions ($\text{Fe}(\text{II})$, $\text{Fe}(\text{III})$). The possible accumulation of (water dissolved) hydrogen and oxygen near the steel substrate (depending on the polarisation history of the steel substrate) might create a kind of additional charge capacity effect, apart from the charge capacity effect of the rust layer.

The hydroxide ions on the other hand will be continuously generated if the DC component of the current signal as experienced by the steel substrate is cathodic (negative). This initiates a pH increase near the steel substrate, with the pH front progressing into the soil. As a consequence, the spread resistance around the defect will decrease as the pH front develops. Over time the spread resistance might decrease with a factor 10 or more, depending on the flux of hydroxide ions being generated and on the shape and size of the defect (including thickness of the surrounding PE coating that has remained intact). Hence for a given AC / DC far field potential signal $U_{ff}(t)$ the current towards a defect will increase gradually over time as the spread resistance decreases. The ohmic drop around the defect $U(t) - U_{ff}(t)$ will decrease, leaving a higher driving force $V - U(t)$ available for the electrode reactions.

The initial conductivity of the soil will depend on the soil type and water content. The conductivity is governed by the mobility of ions in the soil. The different anions (e.g. SO_4^{2-} , Cl^- , NO_3^-) and cations (e.g. Na^+ , K^+ , Ca^{2+}) in the soil can be described by a hypothetical set of ions X^+ and Y^- , provided that these ions are given a bulk concentration and mobility that matches the measured soil conductivity.

This brings the total number of species N to be considered in the soil to 6 (table 3).

Species	Charge z_i	Diffusion coefficient D_i [m ² /s]	Concentration c_i [mol / m ³]
O ₂	0	4.00e-010	1.0E-02
H ₂	0	1.00e-009	1.0E-06
OH ⁻	-1	4.00e-010	1.0E+00
X ⁺	+1	2.00e-010	1.221E+01
Y ⁻	-1	2.00e-010	1.121E+01
H ₂ O	0	N/A	5.5E+04

Table 3: multi-ion transport model with indicative bulk ion concentrations for high conductive alkaline soil

The water concentration given in table 3 holds for a saturated soil.

In order to ensure conservation of mass for each species the change of concentration in an infinitesimally small control volume must be equal to the net input:

$$\frac{\partial c_k}{\partial t} = -\bar{\nabla} \cdot \bar{N}_k + R_k \quad (12)$$

with: $\bar{\nabla} \cdot \bar{N}_k$ the divergence of the species flux,

The total flux of a species is given by [5]:

$$\bar{N}_k = -D_k \bar{\nabla} c_k + c_k \bar{v} - z_k F u_k c_k \bar{\nabla} U \quad (13)$$

with: $-D_k \bar{\nabla} c_k$ the contribution of the diffusion;
 $c_k \bar{v}$ the contribution of the convection;
 $-z_k F u_k c_k \bar{\nabla} U$ the contribution of the migration.

The vectorial field $\bar{v}$ represents a possible water flow in the soil.

The unknowns in the mass conservation equations are the ion concentrations and the potential in each point of the solution. Hence, an additional equation, the electro-neutrality condition, is added to the mass conservation equations:

$$\sum_{k=1}^N z_k c_k = 0 \quad (14)$$

The mobility constant (u_k) used in the ion flux formula (13) is defined by Nernst-Einstein relation:

$$u_k = \frac{D_k}{R \cdot T} \quad (15)$$

meaning that u_k can be computed from the diffusion coefficient D_k .

When using the Nernst-Einstein relation $u_k = D_k / RT$, (with R the gas constant $8.31 J mol^{-1} K^{-1}$), to link the ion mobility constant u_k with the ion diffusion coefficient D_k , the theoretical bulk conductivity σ ($\Omega^{-1}m^{-1}$) of a multi-ion system as described by equations (12) to (14) is given by [5]:

$$\sigma = F^2 / RT \sum_k z_k^2 D_k c_k \quad (16)$$

Given the theoretical multi-ion transport conservation equations (12) to (16) the strategy for defining the bulk concentration values for the different species in table 3 is as follows:

- concentration of O_2 is defined according to soil type, depth below soil surface
- concentration of H_2 is zero or insignificantly small
- concentration of OH^- is defined by the pH of the soil
- concentration of X^+ and Y^- are defined in order to match the theoretical soil resistivity from eq. (16) with the measured value in practice

At the steel surface, the flux of species O_2 , H_2 and OH^- (and H_2O) generated by reactions 1 to 6 is imposed. The flux of species X^+ and Y^- at the steel surface is zero since they are not participating in any electrode reaction. At respectable distance for the defect, bulk concentrations are imposed for all species.

Equations (12) to (16) are solved by using a Multi-Dimensional Upwinding Method (MDUM) [6-7].

Computational method

Since the required CPU time for the multi-ion transport simulations is rather significant compared to the CPU time that is required for determining the potential values V_2 and U based on electrode reaction equations (1) to (4), the mathematical model is solved in real time using a double time stepping algorithm.

The electrode reaction model as described by eq. (1) to (11) is solved with a explicit time stepping algorithm that uses time steps in the millisecond order of magnitude. This is referred to as Real Time Scale Modeling (RTSM) simulations. First equations (1) to (4) are solved for the potential values V_2 and U . Next equations (5) to (11) are used to compute the updated value of the compact oxide surface coverage fraction θ , the rust layer thickness d_r and the rust layer concentrations (Fe_2O_3) and ($\text{Fe}(\text{OH})_2$).

After a number of RTSM time steps the flux for species O_2 , H_2 and OH^- as produced / consumed by electrode reactions 1 to 6 is integrated and a multi-ion transport simulation is launched, whereby the concentration profile changes are computed for a time step that is the sum of the RTSM time steps. This is referred to as a Global Time Scale Modeling (GTSM) simulation.

Based upon the result of the GTSM multi-ion transport simulation, the spread resistance around the defect can be (re-)computed, taking into account the updated information of the pH ($=\text{OH}^-$ concentration) profile in the soil. The updated value of the spread resistance and concentration values for O_2 , H_2 and OH^- at the steel surface are fed back to the RTSM simulation level for the simulation of the subsequent time steps.

This computational strategy is schematised in figure 3.

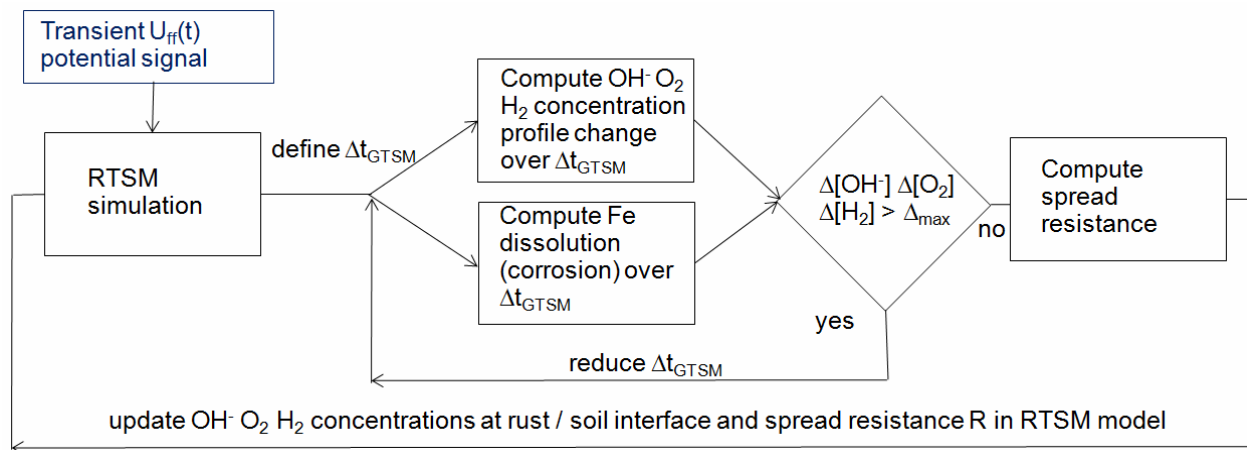


Figure 3: flow chart of computational method

A completely new and dedicated software program ACCorSolver has been developed following the approach outlined above. The software has been fully implemented and validation with laboratory experiments is currently going on. The first results will be presented at the Ceocor congress.

Conclusions

In this paper a time dependant numerical model for the quantification of AC corrosion phenomena has been introduced. The model combines a Real Time Scale Model for solving the electrode reactions with a Global Time Scale Model to solve ion transport in the soil near the defect.

In order to be able to create a numerical model, a coherent set of mathematical conservation equations had to be derived. These equations start from the AC corrosion model that has been developed in the past and for which a number of aspects have been quantified through experiments and theoretical considerations (e.g. the thickness of the compact barrier layers, charge capacity of the rust layer). In order to create a mathematically sound model the following features are added:

- identification of the species that compose the compact barrier layer and porous oxide rust layer;
- introduction of a variable surface fraction $\theta = f(t)$ for describing a compact rust layer that only partially covers the substrate surface;
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A completely new and dedicated software program ACCorSolver has been developed to solve the model described above. The software has been fully implemented and validation with laboratory experiments is currently going on. The first results will be presented at the Ceocor congress.

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