Steps Towards Atmospheric Corrosion Modelling

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Corrosion modeling has been done for several years aiming to provide practical information to corrosion engineers in view of lifetime predictions. The first atmospheric corrosion models were based on fitted correlations with limited or no physical background. Today the increased knowledge on corrosion mechanisms allows to take into account important aspects that govern atmospheric corrosion: composition of electrolyte and electrode composition, galvanic coupling of different materials, oxygen access and film thickness variation.

In this contribution we give an overview of available models and modeling approaches. We start with models that only consider current density distributions due to competing reactions (e.g. oxygen reduction/metal oxidation) or galvanic coupling. They are particularly important for large-scale corrosion systems.

Then models that consider transport of ions are presented. They are mainly research tools to obtain quantified mechanistic understand. Particular attention is given to thin water films with varying thickness that influence considerably oxygen transport and distributions of reaction products. The application is related to steel and metallic coatings coupled in several geometrical configurations (scratch, cut edge).

Finally it will be explained how we see an integration of these models together with film-variation models to stepwise improve atmospheric corrosion models.

1. Introduction

Atmospheric corrosion is governed by a complex interaction as is schematically presented in Figure 1. One or several metals are in contact with each other and an electrolyte film. The thickness of this film changes (1) in time and space (orientation, indoor vs. outdoor) due to climate variations like rain, radiation, relative humidity (%RH) and temperature. Also the presence of dust and hygroscopic species plays an importance role to film formation. At the metal electrolyte interfaces electrode reactions (2) take place involving eventually oxide formation/dissolution and precipitation of reaction products. Main electrochemical reactions are metal dissolution and oxygen reduction. These reactions and precipitation reactions depend on the local composition of the electrolyte film (3). The latter depends on the location showing the presence of chlorides, sulphates and potentially other species. All ions influence the conductivity of the film. Finally the interaction of the film with the environment (4) assures access of oxygen and carbon dioxide.

Today not all of these interactions are taken into account and one can distinguish existing models based on the simplifications made. For instance fitted models of the form "removal rate at a given location as function of alloy, time of wetness, and time" that are based on long duration measurements consider for only one alloy all uncontrolled influences at a given location averaged in time. No real predictive power can be expected in case of changing environment or contact with another metal. Alternatively one can study and model corrosion in idealised laboratory conditions such that many of the influencing parameters are made irrelevant. Such models are also incomplete but form building blocks towards prediction tools. In what follow the focus is on corrosion modelling considering imposed film thicknesses. Models for dynamic film variation will be presented in a separated paper. They ultimately need to be coupled with corrosion models.
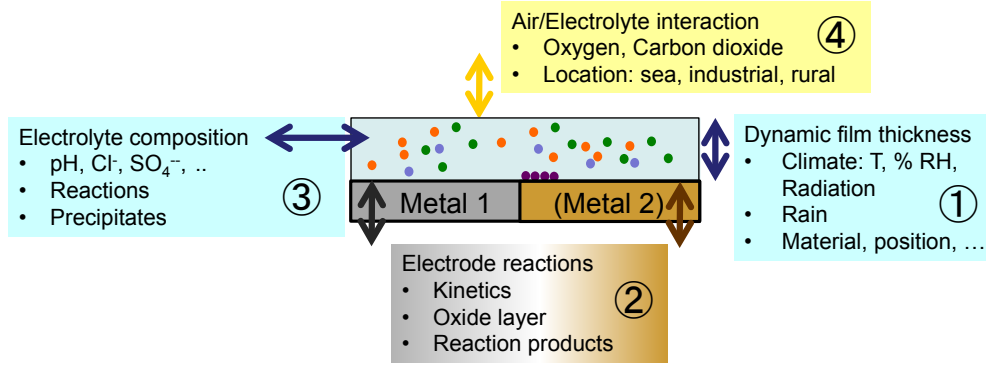
Figure 1: Atmospheric corrosion is the result of a complex interaction between metal(s) in contact with an electrolyte film. This film changes in time (1), electrode reactions (2) take place depending on a changing electrolyte composition (3) and interaction with air (4).

2. Electrochemical models

2.1 Multi-ion model

When an electrolyte film is in contact with metal(s) the following equations describing mass conservation commonly based on dilute solution theory and electroneutrality, are used:

$$\frac{\partial c_i}{\partial t} + \overline{v}.\overline{\nabla}c_i = n_i F \overline{\nabla}.(u_i c_i \overline{\nabla}U) + \overline{\nabla}.(D_i \overline{\nabla}c_i) + R_i \tag{1}$$

$$\sum_i n_i c_i = 0 \tag{2}$$

with c_i the concentration in mol/m^3 of species i, $\overline{v}$ the velocity of the solvent in m/s, n_i the charge number, u_i the mechanical mobility in m^{2}mol/J s , U the potential in V, D_i the diffusion coefficient in m^2/s, F Faraday's constant and R_i the production rate of a species (positive or negative) due to homogeneous reactions including precipitation in the bulk of the solution. Considering that very often no real flow is present in the film but that nevertheless micro-convection is responsible for the formation of a diffusion layer normal to the surface, one can describe the effect of convection by considering an equivalent diffusion that depends on the distance to the wall [Amatore et al., 2001, Dolgikh et al., 2013]. This avoids solving the flow and reduces Eq.(1) to

$$\frac{\partial c_i}{\partial t} = n_i F \overline{\nabla}.(u_i c_i \overline{\nabla}U) + \overline{\nabla}.(D_i + D_{\mu conv}^0 (\delta/\Lambda)^4)\overline{\nabla}c_i) + R_i \tag{3}$$

with $D_{\mu conv}^0$ the diffusion constant of micro-convection, δ the distance to the wall or electrode and Λ a reference distance. At distances larger than Λ the solution may be considered as perfectly mixed.

Along electrodes boundary conditions describing the electrode reactions are imposed. In general these reactions depend to the electrode composition and several reactions occur in parallel. An important example is iron oxidation and oxygen reduction. At the electrolyte-air interface all species have zero flux, except for oxygen and carbon dioxide for which either fixed concentrations either a flux is applied that depends on the oxygen saturation concentration. For stationary simulations on a boundary the concentrations need to be imposed, in contrast to time dependent simulations where only initial concentrations are needed.

2.2 Potential model

When it is assumed that concentration variations may be neglected, Eq.(3) reduces to the following Laplace equation

$$\overline{\nabla}.(-\kappa\overline{\nabla}U) = 0 \tag{4}$$

expressing conservation of current. κ is the electrolyte conductivity in S/m. In Figure 2 we show the modeling results of the galvanic coupling of carbon fiber reinforced polymer (CFRP) and Aluminum AA2024 in a 13 μm thick film of 0.05 M NaCl (Palani et al., 2014).
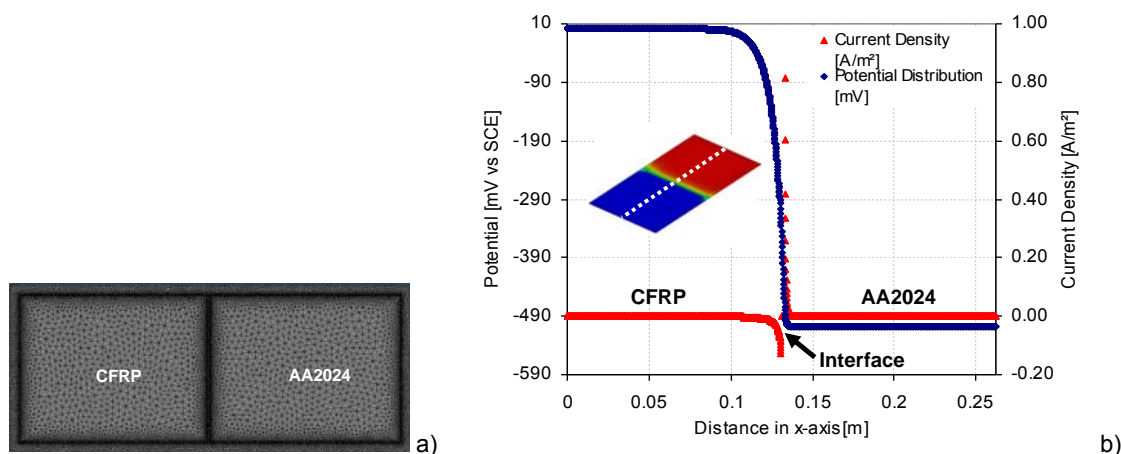

Figure 2: Galvanic coupled CFRP and AA2024 in a 13 μm thin film. a) geometry and mesh distribution. b) current density and potential distribution along the surface. Clearly the current density is localized at the interface.

The driving force being the difference in polarisation of CFRP and AA2024, the current density is limited by the ohmic drop that depends on the conductivity and the small dimensions of the film. Such models are very useful in quantifying worst case scenarios of real industrial situations in three dimensions, like airplane assemblies. The influence of polarisations, film thickness and conductivity, electrode surface configurations, coatings and interelectrode gaps can be quantified, at least at the initial stage. This approach requires that for each combination of electrolyte solution and metal alloy, polarisations curves need to be recorded.

The Laplace equation Eq.(4), is also valid for situations where concentration variations are only confined close to the electrodes such that their effect can be encompassed in the boundary conditions. One can think on offshore applications.

2.3 Potential model combined with oxygen diffusion

In presence of films that are thin, when compared to the dimensions of the surface, one can assume that the oxygen diffusion is only or mainly taking place in the direction of the film thickness between the air and the metal surface. This oxygen diffusion is often the rate-determining step of the cathodic reaction responsible for metal corrosion and two electrode reactions, oxygen reduction and metal oxidation, can be defined now. When applying this rather simple mass transport model with the potential model described in section 2.2, the corrosion rates are influenced by a competition between ohmic and diffusional processes. In this way generalized corrosion combined with galvanic corrosion can be modeled. Although still highly simplified, it provides quantified insight in corrosion risks. Figure 3 shows such a situation where steel is protected by a zinc coating, only in the neighboring region.
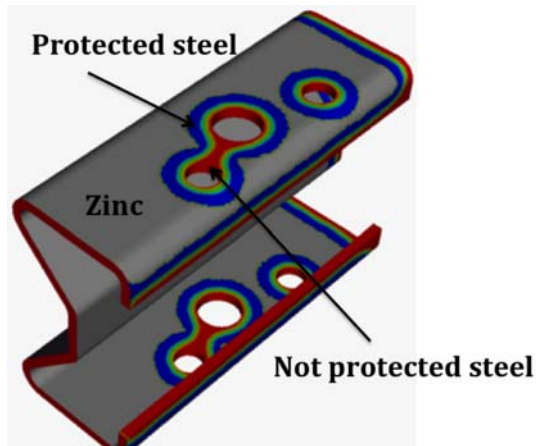
Figure 3: Galvanic and generalized corrosion of steel protected by Zinc in presence of a film of 100µm containing 1% NaCl at pH 7.The zinc being dissolved, after some time the steel is no longer protected, (courtesy Elsyca).

2.4 Multi-ion model for evaporating films

Venkatraman presented in 2011 a model for generalized corrosion depending on the film thickness. In atmospheric or climate chamber conditions the thickness of the electrolyte film on the metal surface is varying in time during evaporation/condensation processes, leading to substantial concentration changes. This makes the potential model inapplicable. The multi-ion model based on Eq.(2) and Eq.(3) needs to be used as the effect of the electrolyte concentration on the oxygen solubility and species transport has to be taken into account. Furthermore these parameters become concentration-dependent.

Figure 4 presents modeling results for the generalized corrosion of steel under a 1% (171 mol m^{-3}) NaCl electrolyte film evaporating from 3 mm down to 100 µm. The corrosion process on steel is controlled by the oxygen reduction reaction. The O_2 concentration at the surface is the result of two phenomena acting in opposite directions: increased oxygen access due to the thinner film and decreased oxygen access due to its lower solubility in concentrated electrolytes. Due to the substantial increase of Cl concentration here the latter effect prevails and the corrosion rate J_{corr} decreases with decrease of the electrolyte thickness δ in contrast to what expected from the Fick's law. If the initial salt concentration is low, the change in oxygen solubility is not so pronounced and the electrolyte film thickness plays a major role in the corrosion current.
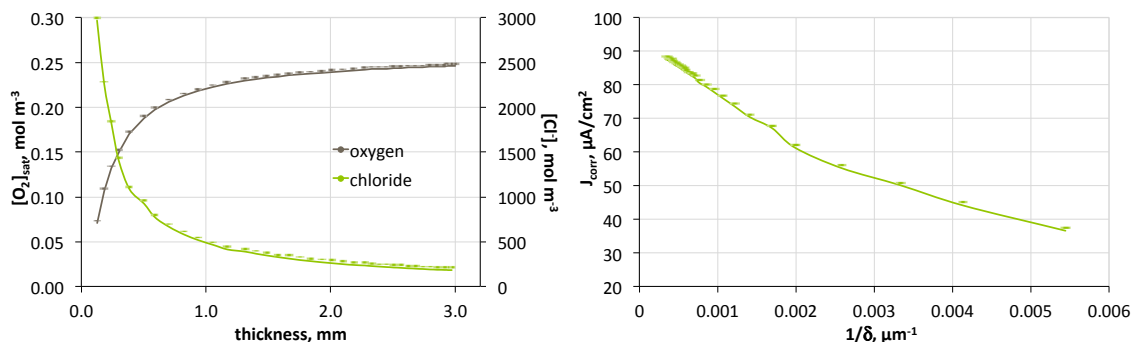

Figure 4: Generalized corrosion of steel under evaporating from 3 mm down to 100 µm 1%NaCl electrolyte film. Chloride concentration increases when the electrolyte film thickness δ is going down, decreasing the solubility of oxygen and the corrosion rate.

2.5 Full multi-ion models

Several authors (e.g. Topa, 2012, Thébault, 2011) presented corrosion modeling taking into account ion transport of many species, based on Eq.(2) and Eq.(3). They wanted to make quantified mechanistic models that reproduce (galvanic) corrosion experiments where current density, oxygen and pH distributions are measured in about 5 mm thick film electrolyte film of fixed composition. Although these films are rather thick, the outcome of experiments and simulation provides very valuable information, also for atmospheric conditions. Figure 5a shows for example the pH distribution around a cut edge of an 800 µm thick steel sheet protected at both sides by a 20 µm thick metallic coating (MC) made of an Al/Zn alloy submerge in a 3 mm thick electrolyte containing 1% NaCl. These alloy show often very active spots

protecting the steel, a situation that is mimicked here by imposing a 100 times more active spot of 1µm on the right MC. Simulations reveal that the activity of such a spot has surprisingly important consequences on the asymmetric pH distribution along the cut edge as well as on the simonkolleite distribution along the steel surface, shown in Figure 5b.
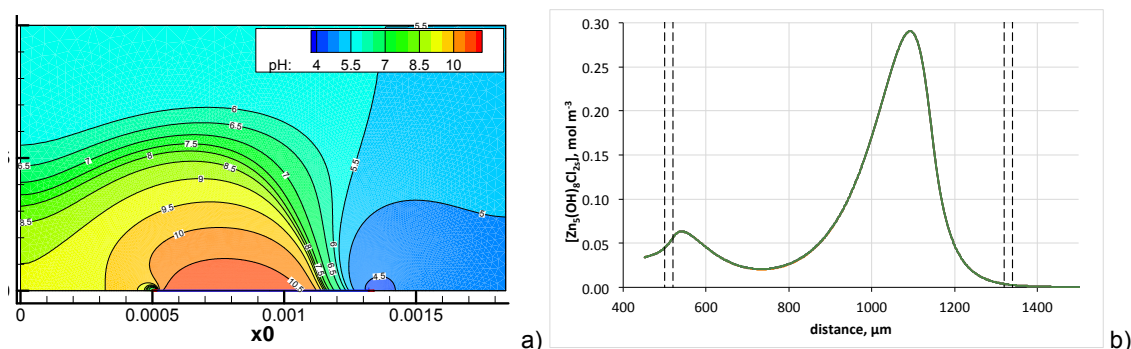

Figure 5: Simulation of the pH distribution around a cut edge of a steel sheet protected at both sides by an Al/Zn metallic coating. At the right coating a small active spot was imposed involving a) an asymmetrical pH and b) simonkolleite distribution.

Such full dimensional simulations be it in two- or three dimensions become difficult when the film thickness becomes smaller than a few tens of microns while at the same time we want to look at surface dimensions of mm. To that purpose dedicated film models are needed as is explained below.

3. Extension towards dedicated film models

Multi-ion models based on Eq.(2) and Eq.(3) consider transport in all directions and involve inherently a discretisation of space in all directions. For very thin film this is no longer needed nor possible and a reduction of *the same* transport equations is made by assuming that transport of species occurs either in the direction normal either in the direction parallel to the surface. For instance *locally* oxygen diffusion is only normal to the surface through the film that nevertheless can vary in thickness along the surface. Both directions remain coupled where needed. Soluble and insoluble species distributions are assumed constant with respect to the film thickness but they can vary along the surface such that galvanic coupling can still be considered. Figure 6 gives a visual representation of the model reduction that we call the Thin Film (TF) Multi-ion Model.
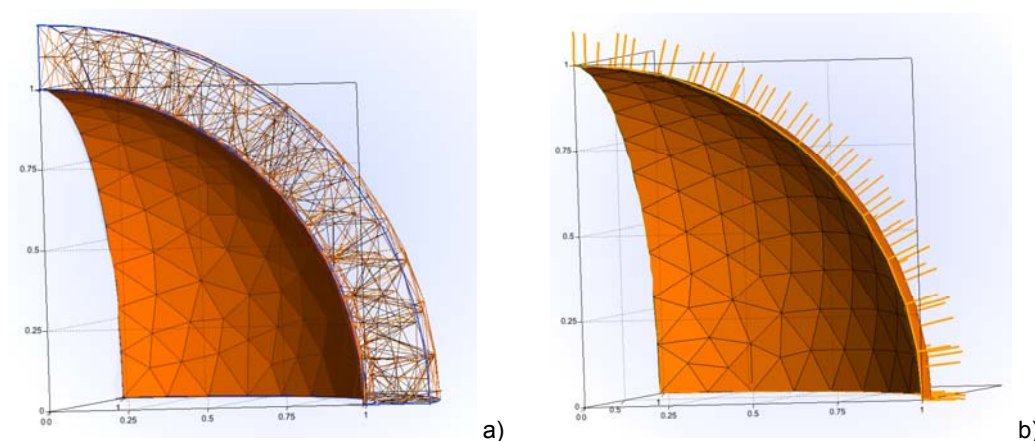

Figure 6: Visualisation of thin film model reduction. A full dimensional model (a) is reduced to a model (b) with transport either in the direction normal to the surface for species like oxygen and carbon dioxide, either in a direction along the surface for species like ions and precipitates.

Precipitated corrosion products can form locally an immobile second phase having a concentration dependent porosity and tortuosity. Also in presence of organic coatings this reduced model can be applied. The coating is to be treated as a second layer in the direction along the surface and transport of many, if not all species, in the coating will become normal to the surface. As mentioned, the film thickness can still

vary along the surface. Using the TF-Multi-ion model it becomes relatively easy to link with separated models describing film thickness variations as a function of environmental changes.

4. Conclusions

We presented in several steps the on-going progress of atmospheric corrosion modelling. There is still much knowledge to be acquired on the detailed corrosion mechanisms involved and on the influencing parameters. But there is no doubt about that this steadily increasing knowledge will be embedded in quantified corrosion models. It is believed that the presented modelling based thin film multi-ion models will gain more and more importance and will become the tool needed for advanced corrosion prediction.

Acknowledgements

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