

Numerical Prediction of Liquid Film Formation During Accelerated Corrosion Tests

Nils Van den Steen*, Johan Deconinck

Vrije Universiteit Brussel, Pleinlaan 2 Brussel, Belgium
 *nivdstee@vub.ac.be

To test new materials and coatings, accelerated corrosion is providing an estimate of the corrosion resistance, protection and evolution. Although the variation of the liquid film thickness and the concentrations of the solutes in the film play a significant role in corrosion processes, little modelling has been done on this subject. Knowing the thickness in every point on the surface would lead to a better understanding of the different processes involved in the corrosion of the metal.

Firstly, a model to predict the time dependent film thickness is presented based on condensation and evaporation processes. The focus being on test chambers, the effect of heat radiation is neglected. The corrosion rate is assumed to be driven by oxygen reduction.

Secondly, using this model, a parameter study is performed by doing three-dimensional simulations on sample plates as used in real experimental tests. The influences of the film thickness and NaCl concentration variation on the corrosion rate are studied as a function of geometrical (surface area, thickness), material (density, thermal properties) and environmental (temperature, relative humidity, fluctuation speed of temperature and relative humidity, heat and mass transfer coefficient) data.

1. Physics, 1D and 3D models

First of all, a one-dimensional model was developed to simulate the evolution of the liquid film. This first model consists of two main components: a heat problem and condensation/evaporation. These two components are linked and therefore can't be solved separately. The driving force behind condensation and evaporation is the temperature difference between the exposed surface of the material and the surrounding air at a certain relative humidity. As the main focus is on climate chambers, the temperature differences are caused by the temperature changes of the surrounding air (convection and conduction). An example of a standardized test is illustrated in Figure 1. At a relative humidity of 100%, even the slightest increase in the air temperature will result in the condensation of water vapour from the air on to the surface. When the humidity is below 100%, a bigger temperature difference is needed to start the condensation process. Hence a time dependent heat problem needs to be solved. In the domain, heat conduction is implemented. Heat conduction,

$$c_p \rho \frac{dT}{dt} = -k \nabla T, \quad (1)$$

follows Fourier's law and depends on the heat conduction coefficient (k), specific heat capacity (c_p) and the density of the material (ρ). The boundary conditions are the heat fluxes (q) due to heat convection

$$q_{conv} = h(T - T_\infty). \quad (2)$$

With h the heat transfer coefficient, T the temperature of the exposed surface and T_∞ the temperature of the air.

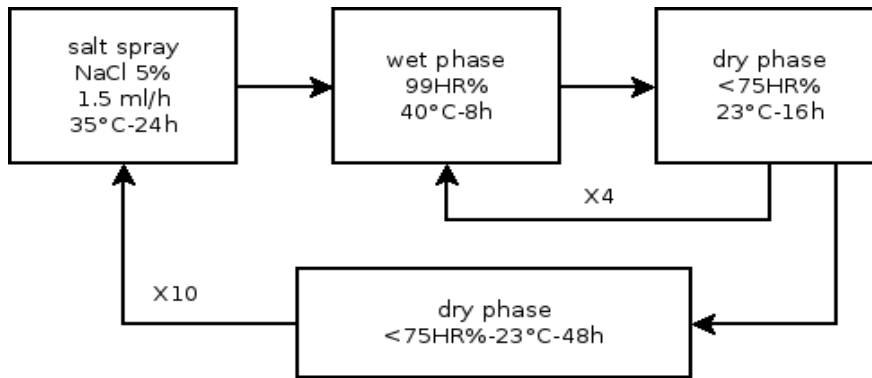


Figure 1: VDA cycle

T is the temperature of the metal at the air/metal interface. In the first stage in the development of the model, the heat convection coefficients (h) are assumed to be constant. The condensation/evaporation mass flux is calculated, using the results from the heat problem. The absolute humidity of the air (w_∞) and the absolute saturated humidity (w) at the surface are calculated. The mass flux of water on the surface is given by:

$$\dot{m} = -k_m(w - w_\infty) \tag{3}$$

and depends on the temperature difference and the mass transfer coefficient (k_m). The condensation/evaporation process is linked with the heat problem by the latent heat (L_v) through equation

$$Q_{latent} = \dot{m} L_v \tag{4}$$

Condensing water will add heat to the material, evaporating water will extract heat. Due to this link, the liquid film can't be computed strictly in post-processing. The limited computational time of this one-dimensional model makes the simulations with this model very suited to get familiar with the problem by playing with the different parameters. A schematic representation of the problem is given in Figure 2. A similar method was used by Baklouti et al. (2001).

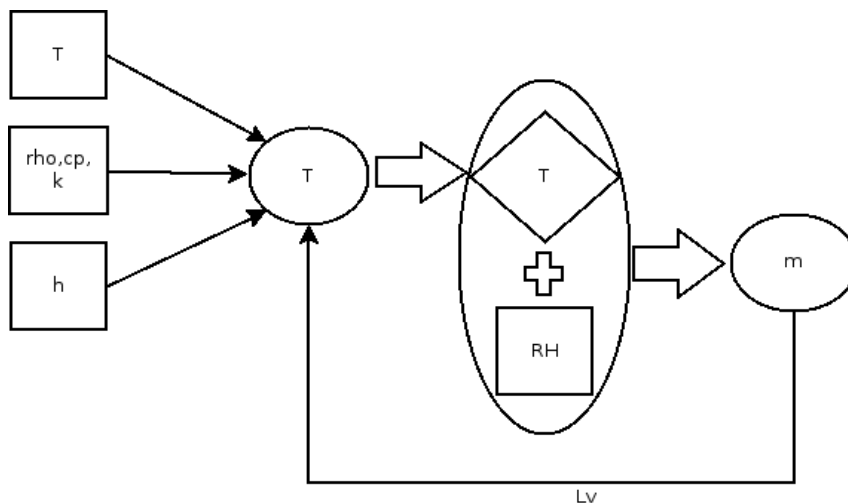


Figure 2: Schematic overview of the calculation procedure

When dealing with outdoor exposure, radiation heat transfer,

$$q_{radiation} = \sigma \epsilon (T_{sky}^4 - T_{surface}^4), \quad (5)$$

becomes significant. The choice to limit the model initially on the liquid film formation in climate chambers was made to maximize the controllability and therefore facilitating future validation.

Next, the one-dimensional model was expanded to a full three-dimensional model. The main difference between the models is the way data (intermediate parameters) are stored. The influence of the main parameters (thickness, specific heat capacity, heat transfer coefficient, ...) was evaluated. This model enables us to compare the different standardized accelerated corrosion tests and to explain the observed differences of the film evolution in time.

This model assumes that film is static, this means it is assumed that the film stays where it condensed. This assumption can be made for thin films, the problem lies with the salt spray phase (for example at the beginning of the VDA cycle (Figure 1)). A solution will have to be found to correctly predict the thickness of the film during this stage. For now, after consulting an experimentalist, a constant film thickness of 100 microns is assumed during the salt spraying.

Another important assumption is made in the formation of liquid films. In this model it is assumed that the film is continuous. In reality however, droplets (Leach et al. 2006) will form on the surface. The droplets will grow until they coalesce and new nucleation centers are created. The goal of this research is to understand and predict the film formation due to condensation and evaporation and make the link with atmospheric corrosion. It is necessary to initially tackle a simplified problem. Once the simplified problem is understood, it is possible to increase the complexity by taken the droplet formation (partially) into account, if this phenomenon proves to be significant.

Dealing with thin films, often the corrosion is limited by the diffusion of oxygen through the liquid film. By taken advantage of this phenomenon, we are able to predict the corrosion currents without much increase in the complexity of the model. Now we are not only able to compare the thicknesses of the film at any given moment, but also to evaluate the corrosion current.

2. Results

A first conclusion that could be made from these one-dimensional simulations is the importance of the thickness of the tested samples. Results of accelerated corrosion tests that are normally performed on thin samples, of which the thicknesses are rarely specified, can apparently be quite different on thick pieces. The thicker the sample is, the more energy is needed to increase the average temperature by one degree. Consequently the time needed to obtain a uniform temperature in the sample, equal to the temperature of the surrounding air, will be increased. As a temperature difference is the driving force behind condensation and evaporation, a different thickness of the sample will result in a different liquid film thickness evolution. In Figures 3 and 4 the simulated (1D) film thickness evolution of samples with four different thicknesses are compared. Figure 3 gives fluctuations of the relative humidity and temperature in time, while Figure 4 gives the thickness resulting from those fluctuations in time. The evolution of the temperature and the relative humidity shown in Figure 3 is used for all the simulations in this work. The values are based on the VDA cycle schematically shown in Figure 1. Because the goal of this paper is to illustrate the film evolution, only a limited version of the cycle is simulated.

During the first period of the test, the salt spray, a constant liquid film thickness of 100µm is assumed regardless the sample thicknesses. On the next stages of the test, it can be observed that the thicker the sample, the thicker the liquid film will be. Another consequence of the thicker film is that it takes longer to completely dry the surface.

The wetted time of the samples with different thicknesses due to the second wet phase starting after 48 hours are compared in table 1. During the wetted time, corrosion will occur.

As mentioned before, when dealing with thin electrolyte films below 250µm, the corrosion current is limited by the oxygen diffusion and thus inversely proportional to the film thickness (Stratmann et al, 1990). Thus a simplified link with the corrosion of the sample can be made without the necessity to solve the differential equations describing the corrosion processes in detail. As the film dries, the corrosion current will increase. Such simplified calculations can be used only for diluted solutions, because decrease of the oxygen solubility has larger effect on the corrosion current than electrolyte thickness. Therefore the corrosion current is limited to 10Am⁻². Considering this simplifications, all the results should be seen as qualitative and in view of comparing relative importance of film variations.

By integrating the current densities, an indication about the corrosion is obtained. It can be observed that the corrosion will be more severe on a thinner sample (5mm or 3mm), despite the lower time of wetness. But we

can observe a limit, as on the 1mm thick sample the charge transfer is lower. The evolution of a liquid film on a 1mm sample will need further investigation as almost no film thickness is observed.

The rate at which the environmental parameters change to their imposed values is another parameter that isn't specified in the standardized test. In Figure 5 the results of three one-dimensional simulations are shown. The sample remains the same in the three simulations (3mm thick steel sample), but the rates at which the air temperature and relative humidity evolves are different: a reference simulation, 50% increase and decrease in the rates (K and % per time unit).

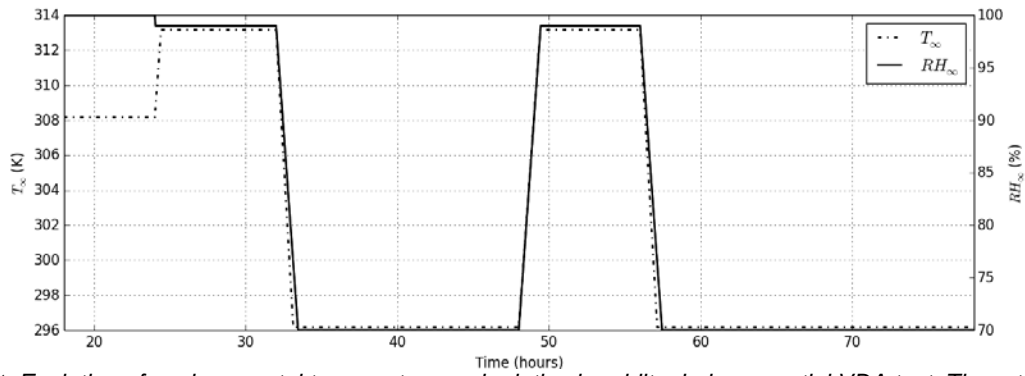


Figure 4: Evolution of environmental temperature and relative humidity during a partial VDA test. The rates at which the temperature changes are 0.5 K min^{-1} and 0.25 K min^{-1} and the rates at which the relative humidity changes are $0.33\% \text{ min}^{-1}$ and $-0.33\% \text{ min}^{-1}$.

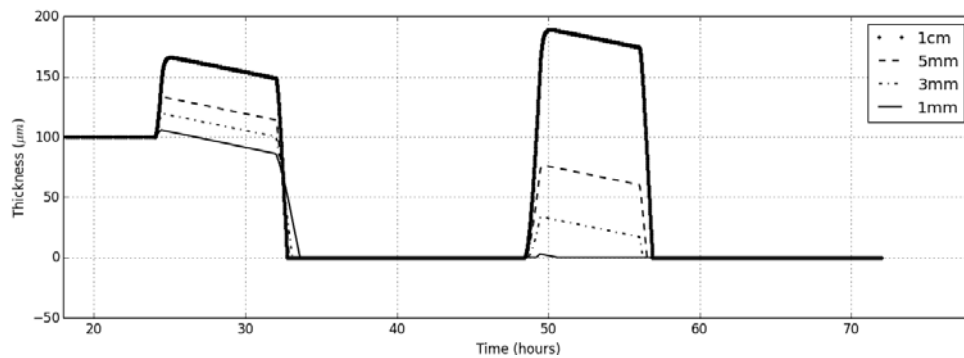


Figure 3: Evolution of the liquid film thickness as function of the metal sample thickness. The imposed air temperature and relative humidity are shown in Figure 3.

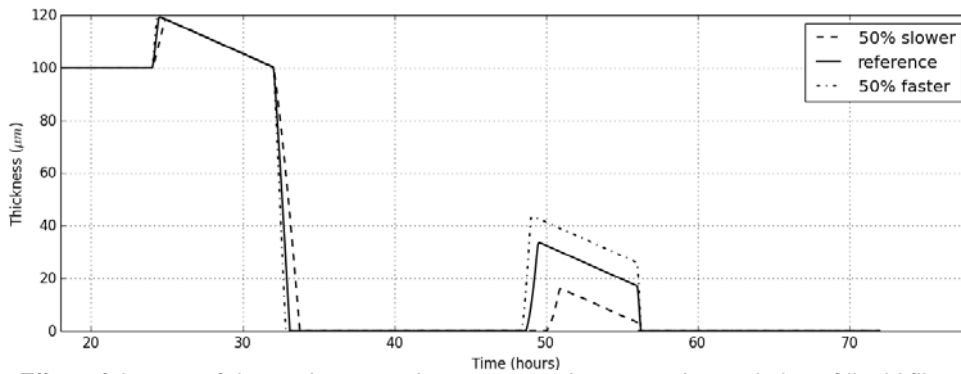


Figure 5: Effect of the rate of the environmental parameters change on the evolution of liquid film thickness on a 3 mm thick sample. The imposed air temperature and relative humidity of the reference are shown in Figure 3.

When the temperature changes quickly, the temperature difference between the surrounding air and the metal surface will be larger compared with slower temperature changes. As this temperature difference is the driving force behind condensation and evaporation, the changes in the liquid film thickness will be larger. Although the period during which the environmental parameters are changing is larger when the rates are lower, this does not fully compensate for the decreased condensation rates. The wetted periods due to the second wet phase which started after 48 hours, are compared in table 1.

Table 1: Wetted time and transferred charges on 100x100mm samples a) different thicknesses subjected to part of a VDA cycle (Figure 3).b) 3mm thick samples subjected to part of a VDA cycle having different temperature and humidity change rates. Reference is shown in Figure 3.

a)			b)		
	Wetted time	Charge/surface		Wetted time	Charge/surface
1cm	8h 26'00"	17 C/m ²	Slow rate	6h06'00"	56 C/m ²
5 mm	8h 01'00"	33 C/m ²	Reference	7h36'30"	68 C/m ²
3 mm	7h 36'00"	68 C/m ²	Fast rate	7h54'00"	61 C/m ²
1 mm	1h 29'00"	15 C/m ²			

Figure 6 compares the calculated corrosion currents of the simulations at different changing rates of the environmental parameters during the wet phase starting after 48hours.

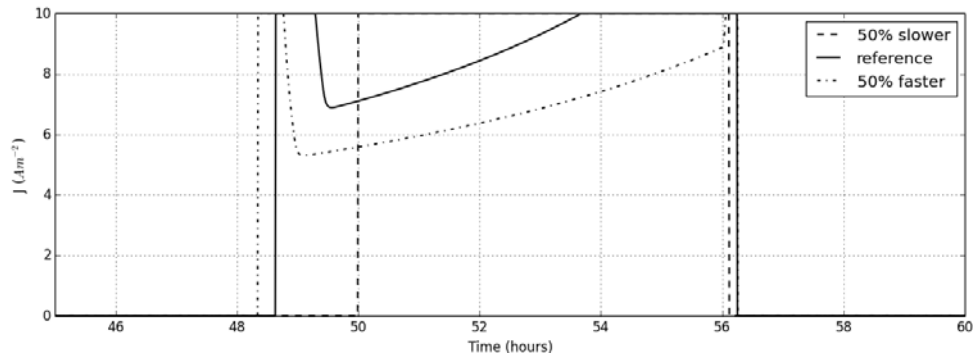


Figure 6: Corrosion currents at different changing rates of the environmental parameters on a 100x100x3mm sample. The evolution of the air temperature and relative humidity of the reference are shown in Figure 3.

In table 1 the surfaces beneath these curves are given. We observe that the corrosion will be more severe in the reference case, despite the lower time of wetness. It should be noted that the chosen current limit will affect these results, especially in case at a slow rate (current limit three times higher results in a charge/surface 2.5 times higher). It can be concluded that the rates at which the environmental parameters change have an impact on the corrosion process.

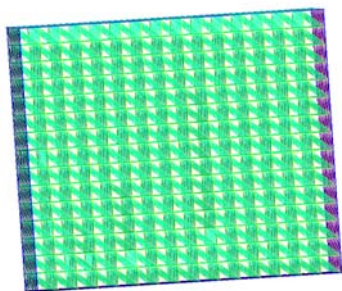


Figure 7: Mesh of 1cm thick sample

The spatial variation of the film thickness on a sample was studied by comparing the film thickness at the center of a sample and at the corner. The differences between these two points depend on the material and environmental parameters, but are small. The mesh used for the three-dimensional simulation is displayed in Figure 7.

In Figure 8 the effect of the heat transfer coefficient is shown. During the simulations, the heat transfer coefficient is assumed to have a constant value. To illustrate the effect, two simulations were performed with a factor 10 difference between the coefficients.

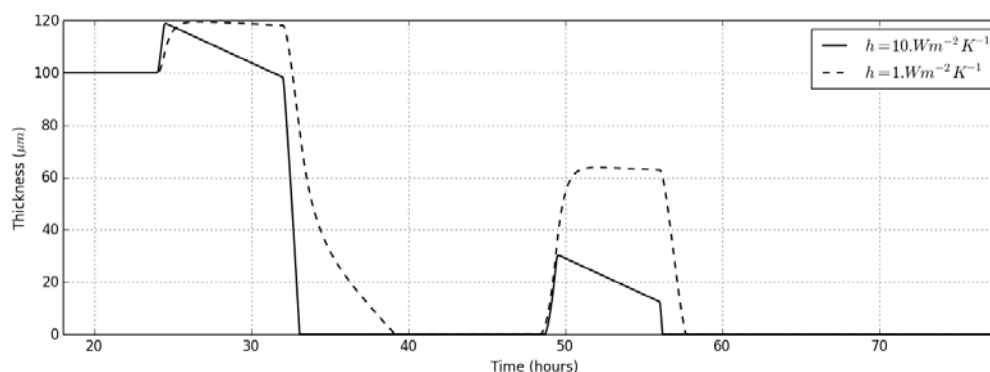


Figure 8: Effect of the heat transfer coefficient on the film formation on a 100x100x3 mm sample during part of a VDA cycle

Two effects are observed: the evolution of the film thicknesses takes longer to reach a maximum and higher values are reached if the heat transfer coefficient is lowered. When the heat transfer coefficient is low, it will take longer for the sample to reach the same temperature as the environment. Because of lower energy transfer due to convection during a certain time, relatively more heat will be transferred as latent heat.

The impact of the specific heat capacity and density (ρc_p) is equivalent with that of the thickness previously discussed.

3. Conclusion

Using a time dependent wetting model for uniform film condensation/evaporation, a study has been performed to identify the significant parameters that influence the corrosion rate. Simulations were performed on steel samples subjected to a part of a VDA cycle.

At constant heat transfer between sample and environment, on thicker samples also thicker films are formed for longer periods of time. However, when considering corrosion that is governed by limiting oxygen diffusion, the corrosion rates of thin samples are more important and obtain a maximum value.

We simulated identical VDA cycles in chambers with different heat transfer coefficients (convection) and observed important differences in film formation and time of wetness. All other parameters being identical, for a sample of 3 mm thick the corrosion rate at low convection ($1 \text{ Wmm}^{-1} \text{ K}^{-1}$) is xx times larger than at a ten times higher convection.

These first results support the need for more elaborated film models that can be linked with detailed corrosion models.

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