COMPUTATIONAL SIMULATION OF GALVANIC CORROSION UNDER THE THIN FILM OF ELECTROLYTE

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Current working practice for the risk analysis of the damage by galvanic corrosion relies on tabulated values of open circuit potentials, the calculation of surface areas of the metals and is largely based on the experience. In this paper a computational simulation of corrosion attack of the constructions that are exposed to the thin film of electrolyte is presented. Theoretical basis of used mathematical model is mentioned. The assumptions for application of the model are discussed. The functionality of used software is demonstrated by modelling of an exemplary situation and by modifications of the input parameters.

Keywords
galvanic corrosion, thin film electrolyte, model, simulation, analysis

1. Introduction

Corrosion is a natural process, which influences all engineering materials. Impacts of corrosion are negative causing technical problems, safety risks and economical losses. Approaches to its restriction insist on the prevention and the control during the design and the lifetime of engineering appliances.

Corrosion has many different forms e.g. uniform, galvanic, crevice, pitting or intergranular corrosion, hydrogen embrittlement etc. [Jones 1996]. Galvanic corrosion occurs when two dissimilar metals are conductively connected in the presence of an electrolyte. Today's technical practice often uses direct connections between different metals considering their mechanical and other properties. At the same time, it is necessary to solve the corrosion aspects of such configurations. Current practice is largely based on the experience. Corrosion specialist has the tabulated values of open circuit potentials and corrosion rates at his disposal. The influence of the geometry is estimated by the calculation of surface areas of the metals.

A possibility of the prevention approach is shown in this paper. A mathematical model of a structure and supposed corrosive environment can be created already as a part of the designing process. Then it is possible to simulate the corrosion attack, find and analyse the critical parts and implement appropriate modifications. Efficiency of such modifications can be proven without expensive corrosion experiments. The determination of corrosion risks can be implemented as a standard part of designing. The simulation is a powerful tool for the corrosion expert solving the critical parts of the constructions.

2. Galvanic corrosion

Galvanic corrosion is a special case of an electrochemical cell. A metal immersed in an electrolyte (the electrode) releases some amount of its cations into the electrolyte and gains a specific value of an electrical potential against the electrolyte. This open circuit potential (OCP) is specific for given combination of the metal and the electrolyte. If two dissimilar metals are immersed into the electrolyte and conductively connected, the metal with the lower OCP acts as an anode. It is oxidized, the dissolution is promoted and the metal corrodes. The metal with the higher OCP acts as a cathode. On the cathode, reduction takes place. In the case of galvanic corrosion it is termed as depolarization.

Electrolyte enables transport of the ions and the conductive connection closes an electric circuit. Electric current flowing between the electrode and the electrolyte causes a shift in the electrode potential. This phenomenon is called polarization. Polarization is a complex phenomenon influenced by kinetics of the processes on the electrode/electrolyte interface [Jones 1996, Schweitzer 2010]. The dependence of electrical potential of an electrode on a current density is called polarization curve. Two conductively connected metals settle their potentials at the same value, called corrosion potential, given besides their OCPs by areas of their surfaces. The areas influence the current density. Between the electrodes flows the corrosion current. OCPs describe the thermodynamics and the polarization curves describe the kinetics of galvanic corrosion.

The evaluation of corrosion is possible in many different ways. Visual evaluation is possible e.g. according to international standard ČSN EN ISO 10289. Quantitative criterion for the evaluation is the mass loss rate and the corrosion rate. In the case of galvanic corrosion this values are connected with the density of corrosion current through the Faraday's law:

$$m = k \cdot q \tag{1}$$

where m is the mass of dissolved metal, k is a factor specific for each metal and q is an electric charge passed through the electrode/electrolyte interface.

3. Thin film

The thin film of electrolyte relates to a situation when the thickness of the electrolyte is much smaller in comparison with a characteristic dimension of the solved problem. Typical example of thin film electrolyte is condensation of moisture or rainfalls running off the constructions. In the bulk electrolyte, corrosion potential is a clear value. Resistance of the thin film has an impact in the thin film electrolyte. Flowing corrosion current causes an unequal distribution of the electrolyte electric potential along the surface of the electrodes. In this paper, software BEASY Corrosion Manager (*http://www.beasy.com)* is used for evaluation of some common structural details. This programme uses BEM approach, as corrosion is a matter of a surface of materials. Analysis of an electrolyte volume is simplified as mentioned below. Physical and mathematical background of the programme is as follows [Palani 2011].

Schematic depiction of galvanic corrosion under the thin film is in Fig. 1:

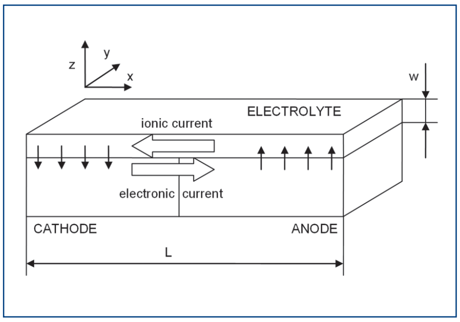

Figure 1. *Schematic depiction of galvanic corrosion under a thin film of electrolyte, under condition w«L*

Equation to be solved is the charge conservation equation in the electrolyte under steady state:

$$\nabla \vec{j} = 0 \tag{2}$$

where

$$\vec{j} = -\sigma \nabla V_e(x)$$

is the corrosion current density, σ is the electrolyte conductivity and Ve(x) is the electric potential in the electrolyte at point $x \in R^3$. The integration domain of the eq. 2 is the volume of the electrolyte.

The boundary conditions for the surface of the electrodes are given:

$$j_n = -\sigma \frac{\partial V_e}{\partial \vec{n}} = f(\Delta V) \quad (3)$$

where j_n is the current density flowing through the surface in normal direction and ΔV is the polarization potential across the electrode/electrolyte interface. Polarization potential is given by $\Delta V = V_e - V_m$ where V_m is the potential of the metal. This boundary condition is described by the corresponding polarization curve for the metal of the anode and of the cathode respectively. These polarization curves must be contained in input data for the simulation.

The boundary conditions for insulating surfaces are $j_n = 0$.

In general, it is necessary to solve this problem in 3D. But if the thickness of the electrolyte w is much smaller than a characteristic dimension of the problem L (see Fig. 1), the electrical potential Ve can be considered as constant in z direction. This behaviour allows excluding the ($\partial j_z/\partial z$) component from the mathematical formulation of the problem by direct integration of it along the thickness w and the eq. 2 changes into:

$$w\nabla_{2D} \cdot \left(-\sigma \nabla_{2D} V_e\right) = -f(\Delta V) \quad (4)$$

where w is the thickness of the electrolyte and ∇_{2D} represents two dimensional *grad* operator acting on *x* and *y* coordinates. The effect of the charge exchange between the anode and the electrolyte or the cathode and the electrolyte is represented as source term and not as a boundary condition. The dimensionality of the problem is lowered from three to two. Even very complex shapes with thin film electrolyte can be solved as 2D problem. Lowering of the dimensionality brings furthermore substantial decrease of the computational demands.

Input data for the simulation programme include 3D model of the part or construction to be solved including the used materials. GiD processor, which is the geometrical interface for BEASY Corrosion Manager, is able to load common formats, such as .IGES or .DFX or create a new geometry. Each surface to be solved must have a uniform layer of an electrolyte assign to it. Solved surfaces are discretized into a mesh of elements, where the programme solves the charge conservation equation. Key inputs connecting the mathematics with reality are the thickness of the layer, the electrical conductivity of the electrolyte and polarization curves measured for given materials and electrolytes. There is a possibility in the programme to include coatings. Each surface can have a coating assigned. The coating is characterized by its ohmic resistance and by the fraction of the whole surface, which has no coating (breakdown factor). This enables to include damaged coatings.

The outputs of the simulation are electrolyte potential distribution and three components of the corrosion current density. Lower potential indicates anodic region and higher possibility of corrosion. Current density in the normal direction gives information about corrosion rate. Positive value of this quantity indicates corrosion. Negative value indicates depolarization reactions. The programme can depict the corrosion attack in the form of corrosion rate or mass loss rate.

4. Example

A screwed joint of two steel plates is modeled as an example. The plates are 100 mm wide and 4 mm thick. The bolts and the nuts are M10. Following figures show a simulation of corrosion attack in the form of corrosion rate (mils per year). Input parameters are changed to demonstrate the influence on the corrosion. Notice the order of magnitude differences of the scales. Fig. 2 shows plates from mild steel and bolts and nuts from galvanized iron. In the model all surfaces are covered with 0.1 mm thick layer of NaCl solution (concentration 1M, conductivity 8.60 S/m). This electrolyte was chosen because it is similar to the solution used during standard corrosion tests. Galvanized iron as a less noble material corrodes. When the surface of less noble material is relatively larger, the corrosion rate is decreased, as can be seen in the Fig. 3 (plates from galvanized iron, bolts and nuts from mild steel). Fig. 4 shows the situation from Fig. 2 but with thinner layer of electrolyte (0.01 mm). The corrosion rate is lower because of higher resistance of the electrolyte layer and the corrosion rate decreases more rapidly with the distance from the material interface. Influence of electrolyte composition can be seen in Fig. 5. Materials used are the same as in the Fig. 2 but 0.1 mm thick layer of tap water (conductivity 0.044 S/m) was used as an electrolyte. The corrosion rate is much lower and more spread along the corroding surface even with comparison with Fig. 4. This is given by higher resistance of the electrolyte layer and by the different polarization curves too. Fig. 6 shows the influence of the

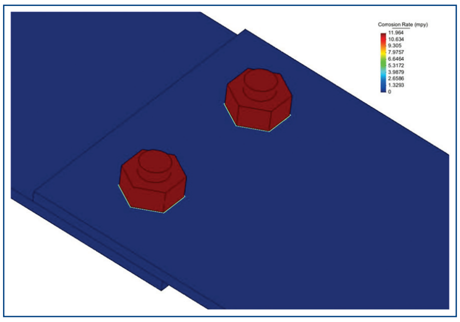

Figure 2. *Plates – mild steel; bolts and nuts – galvanized iron; electrolyte – 1M NaCl, the thickness of the electrolyte layer 0.1mm*

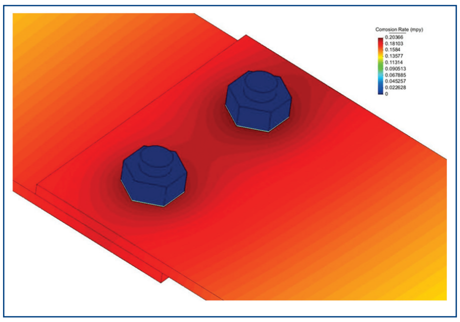

Figure 3. *Plates – galvanized iron; bolts and nuts – mild steel; electrolyte – 1M NaCl, the thickness of the electrolyte layer 0.1mm*

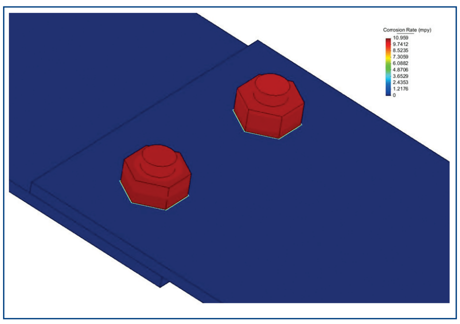

Figure 4. *Plates – mild steel; bolts and nuts – galvanized iron; electrolyte – 1M NaCl, the thickness of the electrolyte layer 0.01mm*

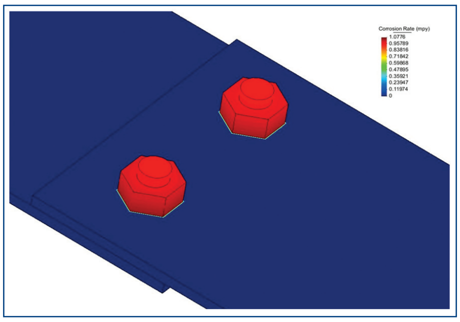

Figure 5. *Plates – mild steel; bolts and nuts – galvanized iron; electrolyte – tap water, the thickness of the electrolyte layer 0.1mm*

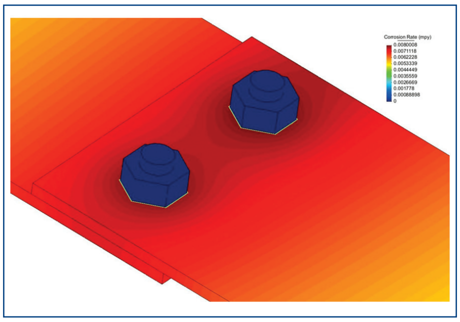

Figure 6. *Plates – mild steel; bolts and nuts – stainless steel; electrolyte – 1M NaCl, the thickness of the electrolyte layer 0.1mm*

materials. The plates are from mild steel and the bolts and the nuts are from stainless steel (304 grade). Electrolyte is 0.1 mm thick layer of NaCl solution. Here the less noble material is mild steel, it has larger surface than the more noble material (stainless steel) and the corrosion rate is the lowest.

5. Discussion

Analysis of corrosion resistance using the corrosion manager consider homogenous layer of electrolyte. Used mathematical model solves the electrical neutrality of the electrolyte layer. Assumption of thin layer allows further simplification and solving the 2D problem. This assumption means that the electrical potential can be considered constant along the thickness of the layer. Here, the thickness of the layer enters into the mathematical treatment of the problem.

BEASY Corrosion Manager does not solve processes during the polarization such as diffusion, migration or chemical reactions. For a given material, the parameters influencing the polarization process are composition of the electrolyte, composition of the atmosphere, which is especially important in the case of the thin layer, and thickness of the layer. Here, the thickness of the layer influences the shape of the polarization curve [Morris 1989, Thébault 2011, Xiao 2012]. Polarization curves have to consider the influence of temperature, which is crucial for the kinetics and influences conductivity of the electrolyte as well. Influence of all these phenomena has to be contained in the polarization curves.

For application of the programme it is necessary to have a large database of polarization curves. Measurement in the thin film of electrolyte is fairly difficult [Stratmann 1990, Liao 2011, Xiao 2012]. Another problem during the application of described program is to determine the properties of the film regarding thickness, conductivity and composition. The thickness and the conductivity are direct inputs and the electrolyte composition determines choice of used polarization curve.

6. Conclusions

BEASY Corrosion Manager is a programme for solving macroscopic problems. It gives information about the risk of galvanic corrosion. Assumption of the thin film electrolyte and mathematical simplification to 2D problem brings lower computational demands. The programme does not solve details of the electrochemical processes. This brings a necessity of large polarization curves database. The main issue during application of the programme is determination of the thin film electrolyte parameters. Even though the determination of input data is exacting process the results of analysis are important for good understanding of corrosion processes. Software analysis can be a useful tool for the materials engineering.

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