

Application of Mathematical Modelling for Simulation of Galvanic Corrosion

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Abstract: This paper deals with an application of mathematical modelling for simulation of galvanic corrosion. A programme for simulation of galvanic corrosion in a thin film electrolyte layer is presented. The programme comprises some mathematical simplifications bringing significant reduction of computational demands and on the other hand a need of specific form of input data. Necessary background for galvanic corrosion is mentioned and the simplifications are described as well as the form of input data. An example of measured input data and their application is shown. Discussion of used assumptions, input data availability and measuring possibilities of the input data is included.

1 INTRODUCTION

Corrosion is significant problem affecting all engineering materials and causing technical problems, safety risks and economical losses. Prevention or reparations are two different approaches to restriction of corrosion impacts. Mathematical modelling is an approach to corrosion prevention, which enables control of an engineering structure with regard to corrosion resistivity already during designing process.

Mathematical model is based on physical description of solved situation and simulation of processes taking place in the system needs appropriate input data. Purpose of this paper is to define input data for simulation of galvanic corrosion and conditions under which they are to be measured. Applicability and limitations due to employed physical model are shown for presented corrosion simulation software.

2 GALVANIC CORROSION

Galvanic corrosion is one form of corrosion occurring when two dissimilar metals are connected in a presence of an electrolyte. Each metal immersed into an electrolyte has unique potential called corrosion potential E_{corr} . If two metals are connected, the potential difference becomes a driving force for a current flowing between the

metals. The electrical circuit closes through the electrolyte. The flowing current called corrosion current I_{corr} (or corrosion current density j_{corr} if converted per unit area) causes dissolution of less noble metal (metal with lower E_{corr}). This metal becomes an anode of an electrochemical corrosion cell. The metal with higher E_{corr} becomes a cathode. On the cathode, depolarization processes proceeds which do not cause the dissolution of the metal. Current flowing between the metal and the electrolyte changes the potential of the metal. The relation between the current density and the potential change is represented by polarization curve.

To predict an impact of galvanic corrosion is difficult because it depends not only on the material properties but also on the geometry of the connection and fast, localized degradation can occur. If more than two materials are connected, the situation becomes very complex.

3 SIMULATION SOFTWARE

Software BEASY Corrosion Manager (CM BEASY Ltd., UK) was used for the simulation. The programme enables to model galvanic corrosion under thin layer of electrolyte. In this context it means, that the thickness of the layer covering modelled structure is much smaller than the characteristic dimension of solved structure. For example atmospheric corrosion can be described as

corrosion in a thin layer of adsorbed moisture or thin layer of electrolyte corresponds with rainfalls covering upper parts of an aircraft fuselage.

Under assumption of thin layer of electrolyte, following steps can be done (Palani 2011) to model galvanic corrosion.

The schematic depiction of galvanic corrosion under the thin film is in Figure 1.

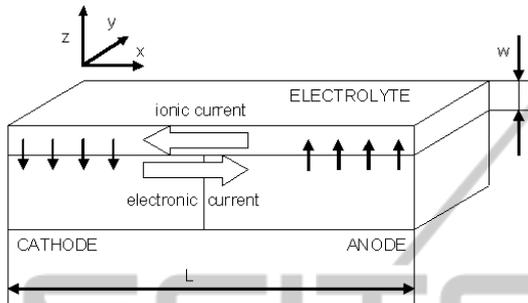


Figure 1: Schematic depiction of galvanic corrosion under a thin film of electrolyte, $w \ll L$.

Equation to be solved is the charge conservation equation in the electrolyte under steady state (1):

$$\nabla \vec{j} = 0 \quad (1)$$

where $\vec{j} = -\sigma \nabla V_e(x)$ is the current density, σ is the electrolyte conductivity and $V_e(x)$ is the electric potential in the electrolyte at point $x \in R^3$. The integration domain of the equation (1) is the volume of the electrolyte.

The boundary conditions for the surface of the anode and of the cathode are given by equation (2):

$$j_n = -\sigma \frac{\partial V_e}{\partial \vec{n}} = f(\Delta V) \quad (2)$$

where j_n is the current density flowing through the surface in normal direction and ΔV is the polarization potential across the metal/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 (see Figure 1), the electrical potential V_e 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 equation (1) changes into equation (3):

$$w \nabla_{2D} \cdot (-\sigma \nabla_{2D} V_e) = -f(\Delta V) \quad (3)$$

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 presented 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 of electrolyte can be solved as 2D problem although this "flat surface" can be twisted in fact. Lowering of the dimensionality brings furthermore substantial decrease of the computational demands.

4 INPUTS

Input data for the mathematical modelling are the geometry of solved structure, the polarization curves of each included material, conductivity of present electrolyte and the thickness of the electrolyte layer.

4.1 Geometry

Geometry of solved structure is the basis of mathematical model. Modelling software BEASY CM uses universal preprocessor GiD (CIMNE, Spain), which enables to create a new geometry or to import an existing geometry in format IGES, DXF, Parasolid, ACIS, VDA, Rhino, or Shapefile. Because the corrosion is a matter of a surface of material, geometry prepared for the simulation of corrosion has to be composed only of surfaces. For the calculations the surface is divided into elements by a discretization mesh. Because the galvanic corrosion takes place in vicinity of different materials interface, the mesh has to be thicken in this areas.

4.2 Polarization Curves Measurement

The key input data for the simulation are the polarization curves. They should be measured under circumstances similar to those causing galvanic corrosion. It requests measuring in thin layers of electrolyte. Thin layer of electrolyte in this context means layer thinner than 100 μm . Such thin layers

results in different polarization processes and different shape of measured polarization curve in comparison with a bulk electrolyte (Xiao 2012). Common term in literature is thin electrolyte layer (TEL).

Polarization curves used for modelling of a structure presented in this paper as an example are shown in Figure 2. Measured polarization curves are modified for the use in the programme. A few discrete points interconnected by lines represent them in the programme. The points for this linearization are shown in Figure 2 too.

Factors influencing the shape of measured polarization curves are the thickness of the layer, chemical composition of the electrolyte and the temperature. Software BEASY CM does not solve processes on the metal/electrolyte interface. Influence of all mechanisms (thermodynamics and kinetics of electrochemical reactions) influencing the resulting shape of the polarization curve has to be included in the measured curves. In dependence on different corrosive conditions to be modelled, there must be accessible a broad database of polarization curves, covering all corrosive conditions for all materials.

4.3 Influence of Coatings

A material with a coating can be modelled as a surface characterized by a new polarization curve. Another approach is included, to use a polarization curve of the plain material and the influence of the coating model by two variables – breakdown factor and ohmic resistance. This possibility is appropriate especially for paints.

Breakdown factor indicates the ratio of area without coating to the total area of a surface. This definition enables to model damaged coatings. Default value is set to 1, describing surface with no coating. Ohmic resistance characterizes the electrical properties of the coating. Default value is set to 0, describing surface with no coating as well.

For coatings capable of electrochemical reactions, typically galvanic coatings, there is a need to measure a new polarization curve of the material with the coating.

4.4 Thickness and Conductivity of TEL

Be the layer of electrolyte thicker than 100 μm or thinner, the thickness of the layer is a part of input data together with electrical conductivity of the electrolyte. For a simulation of atmospheric corrosion very thin adsorbed layers are used with a thickness in the range 10-100 μm (Yadav 2007). If water flowing down or stagnant appears, thicker layers are modelled. The thickness must be measured, calculated (Palani 2011) or estimated. Measured thicknesses for typical situations can be used repeatedly.

Conductivity of the electrolyte depends on the composition. Aqueous solutions are most common although an influence of any type of liquid can be investigated by presented software on principle. Conductivity of aqueous solution depends on an amount of dissolved chemicals (salts, gases etc.). Composition and conductivity of the electrolyte for typical situations should be analyzed and consequently it can be estimated on the basis of similarity.

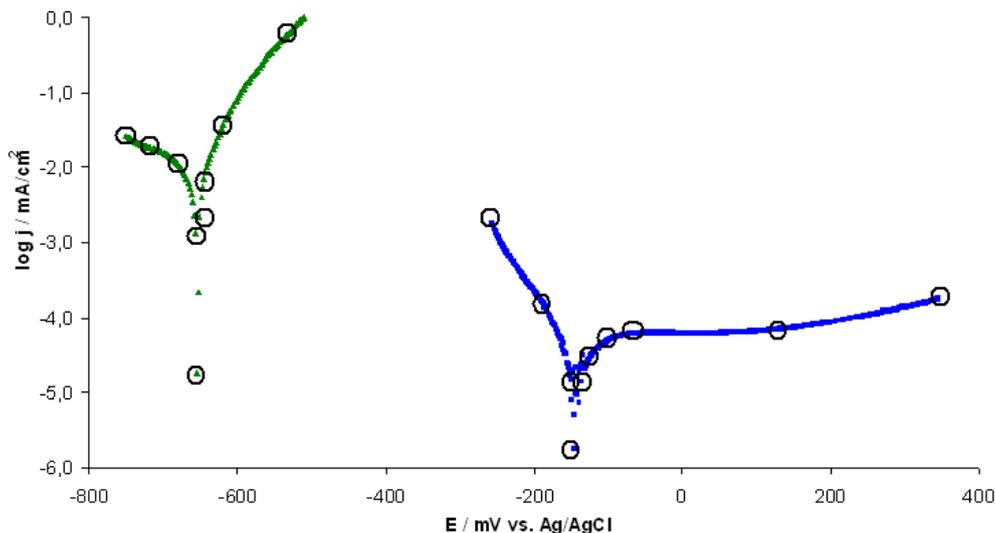


Figure 2: Measured polarization curves in thin layer of water: mild steel – green, stainless steel – blue.

5 OUTPUTS

Results of the calculation are potential and current density distribution over the whole surface of solved structure. Calculated value of current density represents the normal component of total current. This is the current flowing between the metal and the electrolyte, which is the corrosion current. For a visualization of the results postprocessor GiD is used again.

Small construction detail was solved to illustrate the simulation outputs. It is a connection between a hydraulic cylinder and a landing gear of an aircraft. Modelled material composition is shown in Figure 3.

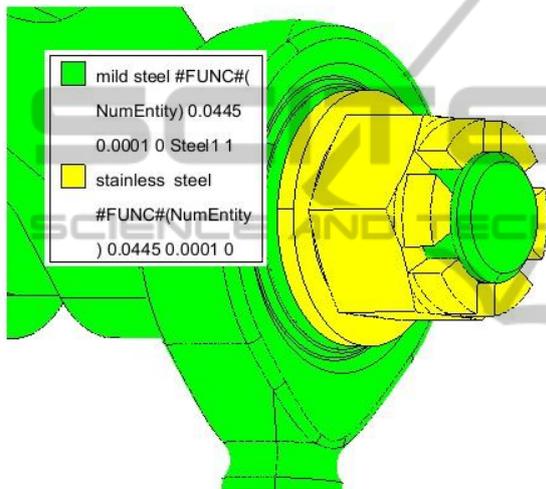


Figure 3: Modelled construction detail and the material composition.

Modelled distribution of potential in the TEL is shown in Figure 4. Solved structure includes two different materials – stainless steel nut and washer and other parts from mild steel. The stainless steel has higher E_{corr} (is electrochemically more noble) and the potential of TEL above the nut corresponds to it. Towards the material interface the potential lowers and above the mild steel parts far from the material interface, the potential of TEL is the lowest.

As an improvement, visualization of corrosion rate was added into the programme. Corrosion rate CR [mpy] (mils per year) is coupled with calculated current density by equation 4.

$$CR = K_1 \frac{j_n}{\rho} EW \quad (4)$$

where $K_1=327.2$ [mm.kg/(A.m.year)] is a constant including Faraday's constant and the unit conversion factor, ρ is the metal density and EW is equivalent weight, characteristic for each material.

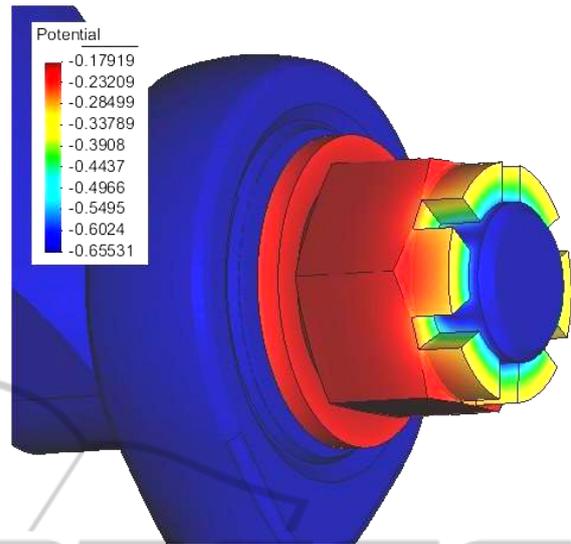


Figure 4: Modelled distribution of potential. Mild steel parts and stainless steel nut in thin layer of water (100 μ m).

Modelled distribution of corrosion rate is shown in Figure 5. The figure clearly shows that the electrochemically less noble mild steel corrodes in the vicinity of the material interface. Distribution of the corrosion rate is not uniform. The highest corrosion rate is near the edges of the stainless steel nut. Material interface between the washer and the loop of the hydraulic cylinder is not visible in the figures.

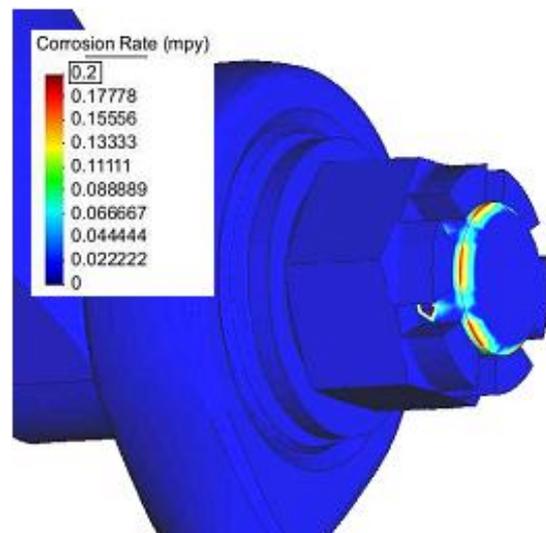


Figure 5: Modelled distribution of CR . Mild steel parts and stainless steel nut in thin layer of water (100 μ m).

Another quantity characterising the intensity of a corrosion attack is mass loss rate MLR [g/(day.m²)] satisfying equation 5.

$$MLR = K_2 j_n EW \quad (5)$$

where $K_2=0.8953$ [g/(A.day)] is a constant including Faraday's constant and the unit conversion factor.

6 DISCUSSION

6.1 Assumptions Discussion

The main assumption used in BEASY CM is the assumption of the thin layer of electrolyte. This assumption enables to treat the volume of the electrolyte as a layer characterized only by the value of its sheet resistance. Currents flowing through the layer in the longitudinal direction cause the continuous distribution of the potential. Mutual interaction between the electrolyte and the material of investigated structure is controlled by the polarization behaviour of the material and is presented in the electrolyte as a source of current (positive or negative). This current flows in normal direction to the surface, represents the corrosion current and is controlled by the local electrolyte potential and corresponding polarization curve.

Flow of the current in the volume of the electrolyte is not solved. This assumption brings mentioned lowering of computational demand, but has to be taken into account, when a real situation is studied. Qualified decision has to be made, if it is possible to model the situation by BEASY CM or not. Critical in this case are fine details with different materials covered by relatively thick layer of electrolyte. This situation is not common in a case of atmospheric corrosion, because the thickness of adsorbed moisture is about 10 – 100 μm . Caution is needed, when a corrosion in thicker layers is modeled, for example the layer of stagnant water covering a part of a car chassis.

Polarization curves are used directly during the calculation as a binding condition between the potential of the electrolyte and the flowing corrosion current. BEASY CM does not solve the mechanisms of polarization. Therefore, the polarization curves have to be measured under conditions as close as possible to those prevailing during the exposition to the corrosive environment. Factors influencing the resulting shape of polarization curve are temperature, composition of the electrolyte, composition of surrounding atmosphere and the thickness of the electrolyte layer. For the simulation of galvanic corrosion by BEASY CM it is necessary to have a database of polarization curves for all included materials covering broad spectrum of

measuring conditions or to have a possibility to arbitrarily measure the curves of included materials for every specific situation which is to be simulated.

6.2 Input Data Discussion

Because there is no comprehensive database of polarization data for materials in TEL in the literature, the measuring of polarization curves is an essential part of using BEASY CM. Because of large serial resistance of the TEL, the measuring in the thin layer requires special techniques. Contactless measurement (Stratmann, 1990) or a special type of corrosion cell (Liu, 2010) are most frequently mentioned in the literature. There is a possibility to measure polarization curves in TEL in Testing Laboratories of Aerospace Research and Test Establishment. The technique is under permanent development and the minimum achievable thickness is decreasing.

As mentioned above, the layer of the electrolyte is characterized with its sheet resistance. This value is given by a conductivity of the electrolyte and the thickness of the layer. Factors influencing the conductivity of an electrolyte are temperature and the composition of the electrolyte.

The main issue during solving a real situation by BEASY CM is to determine the thickness of the electrolyte layer, the composition of the electrolyte and consequently its conductivity and the appropriate polarization curve.

7 CONCLUSIONS

Philosophy of a programme BEASY CM for mathematical modelling of galvanic corrosion was introduced. As a special tool for modelling of galvanic corrosion in TEL, the programme uses mathematical simplifications resulting from physical description of the situation. The programme solves the galvanic corrosion as a 2D problem. This simplification must be considered as a limiting factor, when decision should be made, if the software can be used for modelling of particular situation or not.

On the other hand the programme need special, precisely measured input data. This data are polarization curves measured in TEL and the measuring conditions should cover a broad spectrum of corrosive environments. The other disputable variables are the thickness of TEL and the electrical conductivity of the electrolyte. It is advisable to have a database of the thicknesses and electrolyte

conductivities for typical corrosive environments.

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