

Atmospheric Corrosion Through The Eyes of a Computer Simulation

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ABSTRACT

The economic impact of corrosion on metallic structures is a matter of great relevance throughout the world. More than half of the considerable damage due to corrosion is a result of atmospheric impacts on materials, which is logical considering that the majority of the metallic equipment and structures operate in an atmospheric environment. A need for better understanding of corrosion processes leads to an increased demand for numerical corrosion models, which become increasingly relevant towards simulation, lifetime predictions and optimization of the corrosion prevention.

In the past, atmospheric corrosion has been modeled based on empirical data and statistical considerations. These models provide fitted functions of the corrosion rate or damage as a function of time for different environmental parameters. Nevertheless, the goodness of fit of the experimental data to proposed models depends on many effects such as frequency, duration, type of wetting and drying cycles, and time of year when exposure was initiated. In many cases, these factors are not even considered.

Thus, it is desirable to develop models based on mechanistic considerations, and this paper presents one of such approaches, resulting in the development of a standalone engineering corrosion simulation platform. The ultimate goal of this simulation tool is to predict corrosion risk issues on geometrically challenging and multi-material assemblies prior to their real-life application, taking into account a wide range of factors affecting corrosion severity, e.g. surface area, corrosive environment, temperature, dry/wet cycles, corrosion kinetics, etc.. A step forward has been made, including crevice corrosion simulation that can be used as an input for further evaluation of mechanical properties.

Key words: atmospheric corrosion, corrosion risk assessment, corrosion simulation, corrosion prediction, computer modeling

INTRODUCTION

Atmospheric corrosion is the most destructive type of corrosion that causes serious damage to the metallic structures, vehicles and equipment. This corrosion damage mainly depends on the exposure time and climate factors such as relative humidity, temperature, salinity, time of wetness and presence of pollutants.

In the real-world applications, the atmospheric corrosion phenomenon is even more complex as the exposed assemblies are often composed of joint multi-materials, which are in many cases electrochemically different from each other. This causes a formation of galvanic couples which add another simultaneous corrosion phenomenon. Other than that, depending on the type of metallic material used, a risk of localized corrosion – pitting and/or crevice corrosion – should be considered as well. All three result in an inherent unpredictability in the initiation and propagation of corrosion events and an extremely complex corrosion system to be understood.

Mathematical and computational modeling of corrosion, along with controlled or accelerated laboratory experiments, can yield considerable insights into the role of various compositional, environmental and processing variables on the corrosion behavior of mixed-material assemblies.¹⁻⁷ Such insights can then lead towards the development of improved processing techniques, or design of material microstructure. In this context, mechanistic models of corrosion evolution, based on the mass transport and charge balance equations in multiphase domains, can provide a great opportunity. However, these mechanisms present significant mathematical and numerical challenges that start from the definition of one adequate corrosion simulation model, which does not exist.

Empirical models can be used to predict performance within parameter space for which they are created. Such models can provide an insight into the types of mechanisms that might be dominating the corrosion process, but further dissection of controlling factors is much more difficult. Numerical modeling in which the concentration, potential and current distribution are calculated, plays a role in helping to understand those controlling factors. Among the models used, the Finite Element Method (FEM) has been most widely employed to investigate systems undergoing transport phenomena.

The FEM uses a new and unique thin film approach, compromising an analysis based on a constant film thickness and constant film conductivity (derived from the environmental parameters), and a potential method approach that models the gradient of the electrolyte (corrosive liquid) potential in relation to the distance to the metal surface. Thus, it gives a possibility to model different corrosion scenarios related to a metallic material's intended usage environment and evaluate the harshness of different corrosion effects.

Development of such reliable mathematical models and simulations is an essential part of the future predictive design and maintenance concepts. These models would deliver information about onset and evolution of corrosion and, thereby, fill the gap between corrosion monitoring and estimation of its structural impact from compositional, environmental and processing conditions.

Computational modeling can also play an important role in improving the understanding of localized corrosion processes, in particular when it is coupled with the experimental research that accurately quantifies the important characteristics that control corrosion rate and resultant morphology. Furthermore, a numerical simulation approach can greatly assist in investigating corrosion fatigue and establishing the baseline for life prediction of both critical and non-critical materials.

MACROSCALE SIMULATION

Galvanic corrosion simulation

A simulation technology for predicting galvanic corrosion on mixed metal and geometrically complex assemblies was presented in 2012.² The in-house developed software tool was dedicated to engineers who, based on the beforehand prepared materials database, could create a virtual performance of their real-life assembly in its corrosive environment. The outcome of the predictive galvanic corrosion simulation illustrated areas of the galvanic corrosion risks and associated corrosion rates.

The entire simulation idea is based on a material database, which is created using design of experiments (DoE) by measuring polarization curves in a laboratory setting. These experiments aim to gather electrochemical information on the corrosion kinetics of the specific substrate material exposed to the anticipated operational corrosive environment. The in-house developed software tool uses the generated lab data as a direct input for the predictive modeling (Figure 1). Thus, not only corrosion potentials of the metallic materials (as per galvanic series charts) are used to identify corrosion risk surface areas (which in many cases are inadequate to the corrosion system), but also anodic and cathodic reaction rates are simulated for obtaining corrosion rates that are useful for the design engineer.

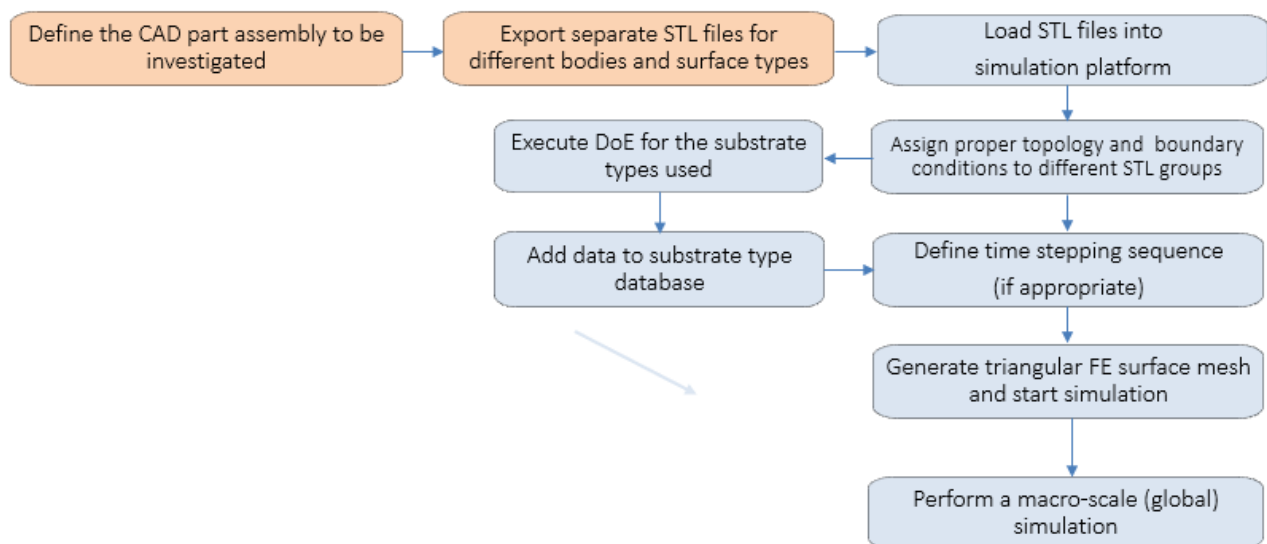


Figure 1: Typical simulation workflow for galvanic predictive modeling. STL stands for a file format native to the stereolithography CAD software created by 3D Systems.

The FEA (Finite Element Analysis) method is employed to solve the fundamental electrochemical equations that govern the corrosion phenomena. These take into account the following:

- LaPlace's equation for potential distribution in the electrolyte with a given conductivity,
- Ohm's law, linking the electrolyte potential with the current density,
- polarization behavior, linking the electrolyte and metal potentials with the current density,
- Faraday's law, calculating the corrosion rate for a given time period as a function of the local current density.

Based on the complex and multi-material model of the ball inlet valve part used on fire engines to control the water flow into the pump (Figure 2), it has been demonstrated that the developed software tool can accurately predict the galvanic corrosion risk areas and therefore, is of a great assistance in quick and proper material selection at the design stage.

Engineering requirements and expectations towards predictive corrosion modeling have greatly increased since 2012, creating a need for further development of the software functionalities. This brought the motivation to extend the galvanic simulation module of atmospheric corrosion simulation, allowing engineers to model the environmental impact as well.

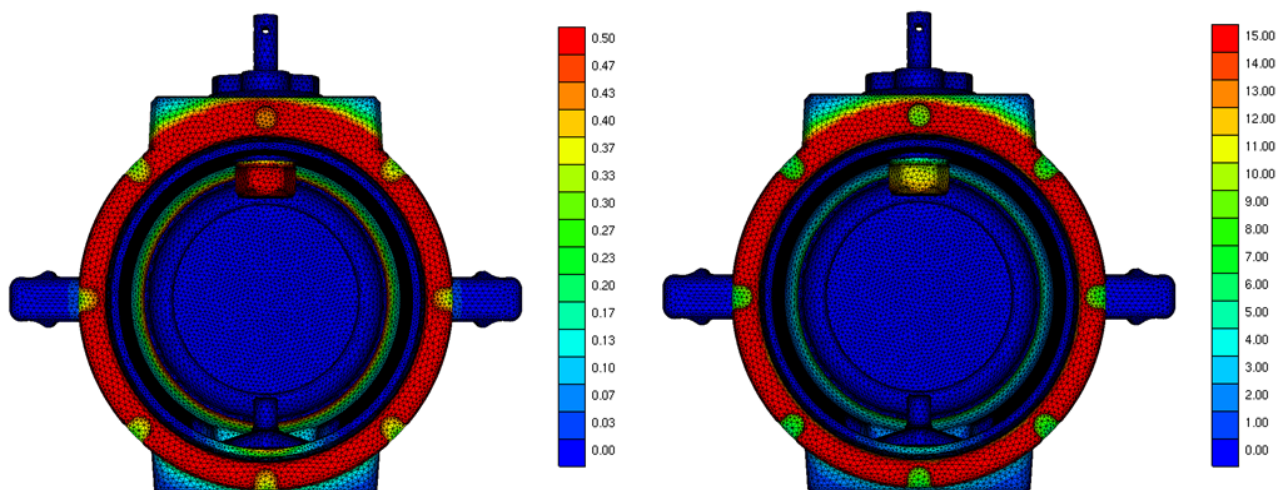


Figure 2: Simulated corrosion rates of multi-material ball intake valve operating in tap water (left) and seawater (right).

Atmospheric corrosion simulation

Atmospheric corrosion is in principle similar to the galvanic corrosion but instead of a corrosion cell where anode and cathode are defined by two electrochemically different interconnected metals, the corrosion cells may originate on the same material as a result of local differences in alloy composition or microstructure, combined with changes in the atmospheric conditions (e.g. temperature, wet/dry cycles, humidity level, etc.). In this respect, the same technology as for galvanic corrosion can be used for atmospheric corrosion. However, in terms of input data, the statistical spread and characteristics of corrosion cells will have to be defined as an input to the model. Moreover, the gathered electrochemical information on the material behavior in its aqueous corrosive environment as obtained for the galvanic corrosion simulation, needs to undergo additional post-processing. This is done by decomposing the “raw” corrosion polarization behavior of a metal substrate into the 3 elementary reaction contributions:

1. Hydrogen evolution: $2\text{H}_2\text{O} + 2\text{e}^- = \text{H}_2 + 2\text{OH}^-$
2. Oxygen reduction: $2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^- = 4\text{OH}^-$
3. Metal oxidation: $\text{Me} = \text{Me}^{\text{x}+} + \text{x}\text{e}^-$

The hydrogen evolution reaction is modeled as a Butler-Volmer type kinetic reaction. The oxygen reduction is modeled as a Butler-Volmer type kinetic reaction with a built-in mass transfer limitation for oxygen supply to the substrate. It is the kinetic parameters of these two reactions that are fit in order to decompose the measured polarization curve into its reaction contributions (Figure 3).