



A PERSPECTIVE TO THE USE OF MULTIPLE TECHNIQUES TO DETECT AND PREDICT CORROSION

Eduardo Gonçalves^a, Luis Filipe Santos^a, Kateryna Popova^b e João Salvador Fernandes^b

^a *Mira Systems Lda, HIESE - Habitat de Inovação Empresarial nos Sectores Estratégicos, Penela, Portugal*

^b *Departamento de Engenharia Química, Instituto Superior Técnico, Av. Rovisco Pais, Lisboa, Portugal*

Abstract: The paper provides an overview of state-of-the-art heuristic approaches to modelling and predicting atmospheric corrosion. Focus is given to the importance of high-quality, real-time input data for achieving accurate and reliable models. Techniques for monitoring environmental and corrosion data are described. Finally, the paper presents a new project combining a novel sensor system with a data-driven predictive model.

1. Introduction

Corrosion is a complex interaction between metallic materials and the surrounding environment, with significant financial, environmental, and cultural implications. Direct global cost of corrosion is estimated to be 3–4 % of global gross domestic product (GDP) [1]. As most metallic structures are exposed to the atmosphere, a large proportion of these costs are due to atmospheric corrosion. Repairing and replacing corroded structures is energy intensive and associated with CO₂ emissions [1]. Undetected corrosion can cause sudden failures, resulting in environmental hazards that endanger health and life. Therefore, researchers worldwide recognize corrosion as an economic, environmental and sustainability challenge.

Studies evaluating the cost of corrosion suggest that implementing available corrosion management techniques could reduce the costs by 15–35 %, while improving sustainability and lowering the environmental impact [1]. Traditional approaches to reducing corrosion include altering the environment, electrochemical corrosion protection, and applying protective coatings. Using predictive models and artificial intelligence for corrosion forecasting is a relatively novel approach to proactive corrosion management that enables material degradation to be predicted before damage occurs. This allows to choose corrosion-resistant materials and select proper maintenance practices and effective designs, reducing unexpected failures and emergency repairs and extending service life. Current corrosion modelling and prediction approaches can be divided into two groups: (i) Heuristic models, which use the correlation between environmental variables and corrosion rates to fit and extrapolate climatic and corrosion data. (ii) Deterministic models, which are based either on approximations of the processes taking place during corrosion or on the results of electrochemical experiments carried out under

controlled laboratory conditions. Although the latter approach provides valuable insights into corrosion processes, it often fails to predict long-term degradation of real structures [2].

This paper therefore reviews state-of-the-art heuristic approaches for predicting atmospheric corrosion of metallic structures in service. It highlights the specifics of atmospheric corrosion as a process to be simulated, reviews the recent predicting models, and describes the techniques for obtaining environmental and corrosion input data. Finally, Section 6 describes a SCOPE project, which aims to combine a novel sensor system with a data-driven predictive model to optimize the inspection and repair management of the coated structures.

2. Atmospheric corrosion

The main factors affecting outdoor atmospheric corrosion include relative humidity (RH), temperature, precipitation, wind direction and speed, and pollutant concentration. Humidity is a key factor, as an electrochemical corrosion process is primarily initiated by moisture deposition in the form of precipitation or condensation. However, defining RH threshold for corrosion activation is not straightforward. A first approximation can be made through the concept of time of wetness (TOW), which defines the time during which the surface is covered with a liquid film capable of causing atmospheric corrosion. According to the ISO 9223 standard, TOW is defined by air RH greater than 80 % at a temperature above 0 °C. Role of temperature is ambiguous due to the complex combination of factors, such as the acceleration of physical processes and chemical reactions, reduction of oxygen solubility in the electrolyte, promotion of electrolyte evaporation, and varying protective ability of precipitated corrosion products [3]. The effect of precipitation can also be rather complex. As the gaseous pollutants, particularly SO₂, tend to concentrate near ground level, dew can be considerably more acidic than rain, which forms at higher altitudes. In contrast, rainfall not only wets the surface, but also has a beneficial effect in leaching and washing the aggressive species and hygroscopic particles from the surface [3]. The effect of wind speed and direction is particularly important in regions close to the ocean or the large industrial plants which produce significant concentrations of corrosive pollutants [3]. Of the pollutants, sulphur dioxide (SO₂) and chlorides (Cl⁻) are known to be the most aggressive towards metallic structures. SO₂ is moderately soluble in water, where it is oxidized to sulphate and increases the acidity of the electrolyte, accelerating corrosion and dissolution of patina layers [2,3]. The primary sources of Cl⁻ are sea aerosols formed by breaking the ocean waves, and traffic on roads where de-icing salts are used in winter. Cl⁻ ion breaks the protective oxide films on metal surface, promotes localized corrosion and attracts moisture [2]. In the advanced stages of the corrosion process, corrosion products begin to play an important role. They can vary significantly in composition, morphology, solubility and adhesion to the metal, and consequently have a complex effect on corrosion kinetics during subsequent exposure [3].

Clearly, atmospheric corrosion is a multiscale, multiphysics process, the kinetics of which are determined by several complex variables. Therefore, understanding and predicting atmospheric corrosion of metallic materials requires detailed knowledge of these parameters and their effect on the corrosion process [2].

3. State-of-the-art heuristic corrosion prediction models

Heuristic models use the correlation between exposure conditions and measured corrosion rates to express the influence of particular parameters, identify the parameters with the greatest effect on corrosion kinetics and extrapolate the results to predict future corrosion behaviour [2].

The long-term corrosion is approximated by time-dependent models, which describe corrosion damage as a function of time using the equations of the following type [2]:

$$C = C_1 t^n, \quad (1)$$

where C is the total accumulated corrosion at time t , C_1 is the corrosion loss after one year, and n is an exponent specific for each material and exposure conditions [2]. These functions are used due to the fact that corrosion rate is usually non-linear and decreases over time due to the formation of corrosion products. More complex approaches can be employed for more precise long-term prediction. For example, Zhi et al. combined a grey Bernoulli model and a genetic algorithm to predict the atmospheric corrosion rate of carbon steel, using data from 16 years of outdoor exposure in China [4].

The first year of accumulated corrosion (C_1) can be related to environmental parameters. So-called dose-response functions use the factors such as temperature (T), RH, TOW, and pollutant deposition, and typically describe C_1 as:

$$C_1 = A_1 + A_2 * TOW + A_3 * RH + A_4 * Cl^- + A_5 * T \quad (1)$$

where the coefficients A_i are fitted constants [2]. According to this model, the dependent variable C_1 is interpreted as a linear combination of a set of climatic parameters. Each independent variable is accompanied by a coefficient indicating its relative weight [5]. The minimum-quadratic regression equation is constructed by estimating the coefficient values to minimise the squared differences between the observed and forecast values, and R^2 statistic is used to assess the model's fit to the experimental data.

Numerous dose-response functions have been proposed for different metals based on the results of site exposures. The ISOCORRAG exposure programme formed the basis for corrosivity classification described in ISO 9223 standard and proposed the damage functions for carbon steel, zinc, copper and aluminum. Mendosa and Corvo proposed corrosion functions based on the atmospheric exposure of carbon steel, copper, zinc and aluminum in Cuba for 6, 12 and 18 months, considering SO_2 and Cl^- deposition, time of rain and TOW as the key factors [6,7]. The International Cooperative Programme (ICP) group developed a model based on exposures at 55 sites in Europe and North America. Corrosion rate was expressed as a function of climatic parameters (T, RH), gaseous pollutants (SO_2 , O_3) and precipitation parameters (average annual precipitation, pH of precipitation and Cl^- concentration in precipitation) [5]. The Ibero-American Atmospheric Corrosion Map (MICAT) programme aimed to develop a mathematical model for calculating corrosion rate in relation to climate and pollution parameters in the region [8]. Pintos et al. applied an artificial neural network (ANN) to develop a carbon steel corrosion prediction model based on the project data, considering TOW, RH, temperature, Cl^- and SO_2 deposition, and precipitation, and reported the superior fitting capabilities compared to the traditional quadratic regression model [9]. Pongsaksawad et al. proposed several prediction models for carbon and weathering steel corrosion in the tropical environment, taking into account T, RH, rainfall, TOW, Cl^- and SO_2 as the key parameters [10]. Chico et al. combined the results of the ISOCORRAG, ICP and MICAT programmes to establish a universal equation for the first year of carbon steel corrosion [5]. They developed damage functions for non-marine and marine atmospheres, identifying temperature, RH and SO_2 in the former, and Cl^- , SO_2 and TOW in the latter as the most significant variables [5].

In the last decade, machine learning algorithms have been used to evaluate more complex and non-linear relationship between environmental parameters and outdoor corrosion rates. Zhi et al. used the Random Forest (RF) algorithm to predict atmospheric corrosion of low-alloy steels, using long-term experimental data from 17 steels at 6 test stations in China and demonstrated how the effect of the environmental factors (Cl^- , SO_2 , RH, T, rainfall and pH of rain) changed with exposure time [11]. Maurya et al. developed an ANN model for predicting zinc corrosion, based on temperature, TOW, exposure time, SO_2 concentration and Cl^- deposition [12]. Terrados-Cristos et al. used the ISOCORRAG data to develop several machine learning

models of galvanized steel corrosion for first-year and long-term corrosion prediction [13]. Halama et al. build an ANN predictive model using the results of long-term carbon steel exposure at three locations in the Czech Republic, with temperature, RH, amount of precipitation, pH of rainfall and SO₂ concentration serving as the input parameters [14]. Chen et al. developed a predictive model for corrosion failure in polyurethane coatings on low-carbon steel [15]. First, the correlations were established between environmental factors and the coating physical properties. Then, the coated samples were exposed to laboratory tests, and their physical properties, as well as the impedance modulus (as an indicator of the coating protective ability) were measured. The environmental factors could then be used to predict the coating protectiveness [15].

All of the aforementioned studies use average annual data as the inputs, and do not consider complex effects of the dynamic environment [16]. The models differ significantly depending on the environment and material, and are only effective under specific conditions [2,9]. Using real-time environmental and corrosion data for the machine learning can provide more detailed information on the corrosion process and more accurate long- and short-term predictions. Pei et al. used galvanic carbon steel/Cu sensors to monitor the effect of environmental parameters on the initial corrosion of steel [17]. Temperature, RH and rainfall were found to be the main factors influencing corrosion. The environmental and corrosion data, together with rust formation parameters, were used as input for an RF corrosion prediction model [18]. One-year monitoring with the same type of sensors confirmed the effect of rainfall and RH and revealed the long-term effect of wind speed, rust layer formation and Cl⁻ accumulation [19]. In another study, the group used hidden Markov models to establish a relationship between galvanic current and environmental parameters and proposed a corrosion index as a combination of environmental variables for quantifying air corrosivity and predicting corrosion [20]. Vangrunderbeek et al. used carbon steel/Cu galvanic sensor to monitor corrosion in accelerated test and used the measured corrosion data and outdoor environmental parameters as input for corrosion prediction by transfer learning [21]. Liu et al. applied polyurethane coating with a defect to carbon steel/graphite galvanic sensor and exposed it to a marine environment for over one year to capture the dynamic environmental effects on coating degradation [22].

4. Environmental data for corrosion prediction models

The quality and time resolution of the input data are key factors in the accuracy of corrosion prediction models. This section focuses on the environmental data used as the independent (“dose”) variables.

4.1 Temperature, RH, wind speed, wind direction and precipitation

The first group of climatic parameters includes temperature, RH, wind speed and direction, and precipitation. These variables can be easily measured in real time and are usually monitored at outdoor corrosion and meteorological stations at a frequency of several minutes.

4.2 Time of wetness

Although the importance of TOW in understanding and predicting atmospheric corrosion is widely accepted, its practical determination varies considerably. The standard TOW definition requires only simple statistical evaluation of temperature and RH data. However, it has been

criticized for excluding the effects of dewing events, the presence of surface wetness at temperatures below 0 °C and the effect of hygroscopic salts and corrosion products.

The temperature of an outdoor exposed metallic structure differs from that of the surrounding air, affecting condensation on its surface [23]. This effect can be accounted for by using surface relative humidity (SRH) instead of air RH as the TOW threshold [23,24]. In this case, the metal surface temperature must be measured in addition to air RH and temperature. Cole et al. performed such measurements on zinc and stainless steel panels and reported that the temperature difference between air and metal was governed by season, wind speed and the level of condensation [25]. Hoseinpoor et al. [23] measured the air and surface temperatures of black and white painted panels and showed that the TOW calculated from SRH was higher than that calculated from air RH, with an annual difference of 33–40 % [23]. Mendoza and Corvo, in their corrosion prediction model for carbon steel and non-ferrous metals, divided TOW into two variables: TOW_{5-25} and TOW_{25-35} , representing the TOW at temperatures of 5–25 °C and 25–35 °C, respectively [6,7]. This approach is based on the observation that dew formation does not occur in the Caribbean at temperatures above 25 °C. Daneshian et al. used the time of condensation defined as the time when the surface temperature fell below the dew point, and found better correlation with corrosion current compared to traditional TOW parameter [26].

Hygroscopic salts present on the surface can absorb moisture at lower RH during wetting and retain moisture for longer time during drying, thus affecting the corrosion process. Cole et al. proposed an estimation of surface wetting based on a comparison of surface RH and deliquescence RH (DRH) of salt contaminants [27].

The surface wetness can also be measured using a sensor. Most of the sensors consist of metal electrodes separated by insulating material [24]. Deposited moisture bridges the insulating gap and causes a change in electrical properties. TOW is then defined as the time during which a certain voltage, current, or impedance threshold is exceeded. Pongsaksawad et al. used an Fe-Ag galvanic sensor to monitor TOW at 7 outdoor sites in Thailand [10]. The authors reported that, at the sites with low pollutant concentrations, the TOW measured with the sensor was equivalent to the ISO definition. However, at the test site with high Cl^- concentration, the measured TOW was almost double the ISO-defined value [10].

4.3 SO₂ deposition rate

ISO 9225 standard defines three procedures for measuring SO₂ deposition rate. Annexes A and B describe the deposition rate measurement on lead dioxide sulfation plate or cylinder. These methods are based on the reaction between atmospheric SO₂ and PbO₂, which results in the formation of lead sulphate. Annex C describes the SO₂ deposition rate evaluation on alkaline surfaces. This method is based on the accumulation of acidic sulphur oxides on the surfaces of porous plates soaked in saturated Na₂CO₃ or K₂CO₃ solutions. Of these methods, PbO₂ plates are most used. The recommended sampling duration for all three methods is 30 ± 2 days. After the exposure, the samples are taken to the laboratory, where the sulphate content and the amount of deposited SO₂ is measured analytically. The main drawback of the measurement is that it requires a lot of manual work including sample preparation, installation, de-installation and sulphate analysis, yet only provides average monthly data.

Although real-time measurement of atmospheric SO₂ concentration is rather simple and is widely used in meteorological and ecological studies and industrial practice, the correlation between atmospheric SO₂ concentration and its deposition rate on a corroding metallic surface is complex. For this reason, there are no reports in the literature of real-time SO₂ deposition monitoring or the application of real-time air SO₂ concentration in corrosion modelling.

4.4 Chloride deposition rate

Chloride deposition rate is measured according to ISO 9225 standard, using either the wet candle or dry plate method. The wet candle consists of two parts. The upper part is a plastic pipe covered with gauze to capture aerosol chlorides, while the lower part contains a glycerol/distilled water mixture reservoir to keep the gauze wet. Glycerol is added to the water to prevent evaporation. In the dry plate method, a dry gauze is fixed to a frame and exposed horizontally under a shelter. After exposure, chlorides are extracted from the gauze into distilled water in laboratory for analysis. As for the SO₂, Cl⁻ deposition measurement requires a lot of manual work and operational steps, while only providing average monthly data.

Pham et al. introduced the concept of the water candle: a device similar to the wet candle, but using a thin water film instead of gauze, which can measure the real-time Cl⁻ deposition rate [28]. The device consists of a glass pipe, a beaker with glycerol/distilled water solution, a pump, and a conductivity sensor. The pump circulates the solution from the beaker to the glass pipe, creating a thin water film on its outer surface, on which chloride-containing aerosol is captured. The conductivity of the solution increases with the increasing Cl⁻ concentration. The device was successfully tested in laboratory and installed on a bridge for one week. The cumulative result after the field exposure corresponded well with wet candle and wind speed. However, the authors reported significant solution evaporation despite the addition of 40 % glycerol, and the need to add the solution daily. As the conductivity measurement was not ion-selective, and other species may have increased the solution conductivity and interfered with the results.

5. Corrosion rate measurement

The corrosion response of the material, most frequently expressed in terms of corrosion rate, is the key dependent variable and output in the prediction models. This section reviews the techniques for average and real-time corrosion rate evaluation in the field.

5.1 Standard coupons

The average corrosion rate can be evaluated by measuring mass loss of metal coupons after outdoor exposure according to ISO 9225 standard. Mass loss is obtained by removing corrosion products after exposure, either mechanically, chemically or both. The advantages of this technique include its ease of interpretation, versatility and low price. However, the measurement is time consuming and does not allow for real-time monitoring [29].

5.2 Galvanic corrosion sensor

Galvanic sensor consists of two different metal electrodes initially insulated from each other. One metal is a noble metal acting as a cathode, the other is the metal of interest which corrodes during the measurement and thus becomes an anode. At high RH, a thin conductive layer of electrolyte condensed on the sensor connects the electrodes, and galvanic current proportional to corrosion current and therefore related to the corrosion rate is generated [29]. Although galvanic coupling with the noble cathode accelerates corrosion of the anodic metal, Pei et al. and Li et al. calculated the influence of the galvanic cell for a carbon steel/Cu coupling and reported the maximum effect to be 10–14.4 % of the natural steel corrosion rate [17,19]. Liu et al. used the technique to monitor and predict corrosion of a coated sensor with an artificial defect [22].

During data interpretation, careful consideration must be given to the effects of precipitation, dew and corrosion product formation, as these events induce an additional current that does not correspond to an increase in corrosion rate and must be corrected. Another disadvantage of the galvanic sensor is its dependence on the presence of electrolyte layer. Pei et al. calculated the lowest detectable steel corrosion rate to be $60 \text{ g m}^{-2} \text{ year}^{-1}$, which corresponds to C2 corrosivity class according to ISO 9223 standard [17]. Advantages of the technique include insensitivity to temperature variations, good correlation with coupon mass loss and real-time results.

5.3 Electrochemical techniques

As corrosion is an electrochemical process in its nature, the corrosion rates can be determined by electrochemical techniques such as electrochemical impedance spectroscopy (EIS) and electrochemical noise (EN) [29]. EIS is a non-destructive technique that provides information about corrosion mechanism and protective effectiveness of coatings by studying capacitive, inductive and diffusion processes taking place in the electrolyte/metal (electrolyte/coating/metal) system. Measurement is based on applying a low amplitude alternating voltage in an electrochemical cell and recording the current response as impedance spectra at a range of frequencies. The data are analysed by fitting to equivalent circuits as analogues that reproduce the electrical properties of the system. However, the correct fitting and data analysis are time-consuming and require experience and detailed knowledge of the system [29]. EN is a term generally used to describe the current or potential fluctuations that occur on a corroding electrode. EN does not disturb the system during the measurement, is easy to set up and suitable for in situ measurements. However, the results require complex interpretation, and there is no generally accepted method for direct corrosion rate calculation from the EN signal. Both methods require the presence of an electrolyte layer to provide conductive connection between the electrodes. In atmospheric corrosion studies, this can be achieved by natural condensation or by using a filter paper soaked in electrolyte or a gel electrolyte placed between the electrodes. However, in the first case the measurement can be interrupted in a relatively dry environment and under discontinuous electrolyte, while in the second case, the additional electrolyte affects the environment and can accelerate corrosion [29].

5.4 Resistometric technique

The resistometric technique is based on recording the electrical resistance of a metal conductor exposed to corrosive environment [29]. As the conductor corrodes, its resistance increases as the cross-sectional area is reduced. As resistance also depends on temperature fluctuations, the sensor usually includes a reference part used to compensate for the temperature effect. The corrosion depth of the actively corroding measuring part can then be calculated from the difference between the initial and actual electrical resistance values of the measuring and reference parts. Alongside monitoring the corrosion of bare metals, Diler et al. [30], Zajec et al. [31] and Popova et al. [32] presented the application of the sensors for corrosion monitoring of coated materials.

Resistometric sensors are simple to install and operate, require little maintenance and provide easy-to-interpret, real-time data. However, the results are affected by localized corrosion, which can lead to incorrect corrosion rate assessment. Therefore, resistometric sensors have traditionally been used to detect uniform corrosion. Another drawback of the technique is its sensitivity to temperature fluctuations.

5.5 Eddy current

Eddy current is an electromagnetic technique based on the principle of electromagnetic induction [33]. When a magnetic field is established in a coil, it induces eddy currents on the surface of the adjacent material perpendicular to the coil. These currents then generate their own magnetic field, which opposes the primary field. The technique has been used to characterize the microstructure of metallic materials, distinguish between pure materials and alloy compositions, determine material hardness after heat treatment and detect residual stresses in engineering structures. It is also used to evaluate the thickness of coatings and oxide layers by measuring the variation in distance between the probe and the substrate. A drawback of the technique is its high susceptibility to temperature variations.

In corrosion studies, the eddy current technique can be used to monitor the evolution of corrosion of a coated metallic structure by placing the sensor between the metal surface and the protective layer [33]. From the perspective of the sensor's exciter coil, the protective layer acts as the metallic target inducing eddy currents. As the structure is exposed to the environment and the coating wears away, changes in its thickness and composition cause changes in the magnetic field of the sensor coil.

6. SCOPE project

As discussed in previous sections, state-of-the-art approaches to the evaluating of environmental and corrosion data and applying them to construct accurate and reliable predictive models are somewhat limited, primarily by the lack of the techniques for real-time SO_2 and Cl^- deposition measurement, and for universal evaluation of the corrosion rates, particularly of coated structures, applicable in atmospheres.

SCOPE (Sensor of Corrosion and Coating Performance) is a new project carried out in collaboration between Mira Systems and Instituto Superior Técnico. It is focused on developing sensors for measuring SO_2 and Cl^- deposition outdoors in real time and on developing a corrosion sensor based on the eddy current technique for real-time monitoring of coating degradation. Based on the results, a novel data-driven model will be built to optimize the inspection and repair management of coated structures in situ, thereby enhancing the cost-efficiency and sustainability of their operation.

7. Conclusions

Based on the provided overview, the following conclusions can be drawn:

1. A variety of corrosion prediction models have been developed over the last few decades, ranging from simple dose-response functions to advanced machine learning approaches.
2. High-quality, real-time environmental and corrosion input data are crucial for building a reliable predictive model.
3. Ambiguous evaluation of TOW and absence of techniques for real-time SO_2 and Cl^- deposition monitoring are critical gaps in the environmental input data. Several techniques exist for evaluating atmospheric corrosion. However, none of these approaches is universal, particularly when it comes to assessing the corrosion degradation of coated structures.
4. The new project aims to address this issue by developing a novel, real-time data driven model for predicting corrosion of coated structures.

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