NOVA

University of Newcastle Research Online

nova.newcastle.edu.au

Melchers, Robert E.; "Using models to interpret data for monitoring and life prediction of deteriorating infrastructure systems". Published in Structure and Infrastructure Engineering: Maintenance, Management, Life-Cycle Design and Performance Vol. 11, Issue 1, p. 63-72 (2015)

Available from: <http://dx.doi.org/10.1080/15732479.2013.879317>

This is an Accepted Manuscript of an article published by Taylor & Francis in Structure and Infrastructure Engineering: Maintenance, Management, Life-Cycle Design and Performance on 03/06/14, available online: <http://www.tandfonline.com/10.1080/15732479.2013.879317>

Accessed from: <http://hdl.handle.net/1959.13/1055051>

Using models to interpret data for monitoring and life prediction of deteriorating infrastructure systems

Robert E. Melchers*

Centre for Infrastructure Performance and Reliability, The University of Newcastle, Callaghan 2308, Australia

(Received 6 November 2013; accepted 20 December 2013)

For environmental and for economic reasons, there is increased emphasis on extending the life of existing infrastructure and to design new infrastructure for longer, safe and effective service lives. Increasing use is being made of monitoring of performance and estimation of long-term reliability and safety, allowing also for the likelihood of long-term deterioration. To obtain optimal decision outcomes, reliance should be placed not only on data but also on accumulated scientific and engineering knowledge. In engineering, this is embodied in mathematical models. Ideally, these are of good quality, calibrated to 'real world' data and have prediction capabilities. Recently, developed models of this type are described for the corrosion of steel in marine environments and simplified to models suitable for engineering applications. An example is given of the prediction of the expected corrosion loss and of the likely future rate of corrosion for a mild steel structural element exposed to temperate seawater.

Keywords: corrosion; models; prediction; probability; remaining life; steel

1. Introduction

Technical and managerial decisions about the adequacy of current and the likely future performance of physical infrastructure items, both new and old, is of much interest, largely for reasons of economic rationality (Paik & Melchers, 2008). Industrial infrastructure often is constructed from steel and particularly in or near marine environments likely future corrosion, and hence, safety and performance is an important technical issue. Examples include marine applications, such as offshore and harbour structures and facilities, pipelines and shipping (Committee, 2006). Protective coatings and cathodic protection are widely used, and when properly applied and maintained, can provide excellent long-term protection. In practice, this ideal is not always attained, such as through lack of timely maintenance or lack of funding when required or, worse, lack of understanding of the basic requirements. As a result, there is ample evidence in practice of older steel infrastructure showing moderate or even severe corrosion. There are also some situations for which protective coatings last a very short time and cathodic protection ineffective or technically impractical. Examples include mooring chains, water injection pipelines, the interior of bulk carrier ships and the exterior of pipes buried in soil for extended periods of time. For operators, engineers, managers and owners of a physical infrastructure asset, important questions about the management of the asset include: (1) is it safe, (2) for how much longer will it remain safe and (3) at what cost?

Additionally, for 'safety', can performance or some other criterion be substituted? Usually, these are difficult questions, although technical techniques such as structural reliability analysis (Melchers, 1999) can be brought to bear on them. By far, the most difficult question is the second, implying a need to predict the future, and this implies that any future rate or degree of deterioration also must be predicted. Once that is known or estimated, the rate of loss of safety or reliability can be estimated and used to help assign priorities for maintenance or replacement. It also can be used to make optimal decisions about which assets to inspect in order to assess their current condition based on probability arguments, rather than using simple time-based inspection systems as is traditional, say, in shipping (Gudze & Melchers, 2008).

In common with structural engineering generally, but at variance with many other engineering fields, the assessment and prediction of the structural safety for an individual asset relies heavily on mathematical models. These are formulations at some degree of professional consensus and are based on theory as developed from past experience and experimental observations. They represent accumulated previous professional and other experience, including lessons learnt from past failures. They are therefore more than a collection of empirical data. This approach provides a user with much greater degree of confidence in the outcomes the models produce and also in their extrapolation to the future. From this, follows the

*Email: rob.melchers@newcastle.edu.au

principal reason for seeking models for deterioration – they incorporate the best information and expertise that is available and allow data interpretation in the light of other knowledge as well as extrapolation based on that knowledge as well as the actual observations.

As implicit in the above, models also can assist in the interpretation of data and the observations obtained in an experimental programme. It can help in deciding whether the experimental observations are reasonable and in accord with past experience. It also can help in interpreting the data for situations in which there is limited previous direct experience but for which mathematical models can be developed from related past experience. These concepts can be illustrated as in Figure 1. Consider the corrosion of some new material as a function of time. After a given amount of time t_i , a degree of corrosion $c(t_i)$ is observed (Figure 1(a)). Because there is no previous experience, the value $c(t_i)$ must be taken as given at this time. The question of interest is the progression of corrosion for $t > t_i$. A related question is whether the rate of increase can be estimated by the extrapolation of $c(t_i)$ from the origin (the ‘apparent corrosion rate’) as would be the usual assumption if no other knowledge were available.

A potentially better estimate of deterioration can be obtained by taking another reading at some point later in

time t_e , as in Figure 1(b). Then, the likely rate of deterioration for $t > t_i$ is given by r_s . This approach relies on the uncertainty in the assessment of $c(t)$ at both observation times t_e and t_i , being sufficiently small to allow sufficient discrimination between them and to permit a reasonable estimate to be made of r_s . Otherwise, the uncertainty in r_s will be very high (Figure 1(c)). Better estimates of r_s can be made by having the observation times t_e and t_i spaced sufficiently far apart in time.

For steel corrosion, for example, this might require several years. This is an obvious disadvantage – usually, the need to estimate future deterioration is immediate and cannot await the outcomes of an investigation extending over several years. Specifically, when deterioration problems are discovered at time t_e and appear serious, the potential risks involved may mean there is little time available for a subsequent inspection and is likely to be made only a relatively short time later, say at t_i . In this case, the readings are too close together relative to the uncertainty in each estimate of $c(t)$ and there will be high degree of uncertainty about the future rate of corrosion (Figure 2(c)). If this approach is adopted, the uncertainty in the estimated rate must be included in any reliability assessment.

If some prior information about the deterioration of the material is available, and formulated as a (‘theoretical’) or

Figure 1. (a) Corrosion loss observation $c(t_i)$ at time t_i and the required long-term rate r_s (b) estimation of the long-term rate r_s from two (or more) observations at t_e and t_i , respectively, (c) as in (b) but with close observations giving high uncertainty in extrapolation, (d) extrapolation based on a known theoretical model and (e) interpretation of observed data (measurements) relative to the underlying model and the correction of apparently misleading data trend.

Figure 2. Model for corrosion showing (a) sequential phases, model parameters (r_0 , c_a , t_a , c_s , r_s) and the early and later influence of nutrient availability levels and (b) effect of increasing water temperature and reducing DO concentration.

underlying mathematical model, the estimate for r_s can be much improved. This is shown schematically in Figure 1(d) by the tangent to the model at t_i . Similarly, if a model is available, it is easier to interpret new data and to ascertain whether it is consistent. An extreme example is shown in Figure 1(e) in which the data suggest a trend opposite to that expected from the model. In this case, the data can be interpreted as having a certain degree of error – this can be used in the development of probabilistic models to estimate model uncertainty (see below).

It is clear from the above that models for deterioration are highly desirable, both to interpret data and to extrapolate any trends the data may have. An overview of the development of a model for the longer-term corrosion of steel in marine environments is given in the next section. Rather than using empirical data alone, the approach uses corrosion science principles and rate-determining processes as the foundation for the model. As will be seen, the model consists of a number of sequential but different rate-controlling processes, and these are influenced in specific ways by the external environment and by internal metal characteristics. This realisation has permitted the interpretation of previously apparently inconsistent data but it is also the key to the interpretation of new data such as might be collected in a new experimental programme or as part of the assessment of an existing structure. The key argument is that understanding generated by the model development provides the means to create better understanding, and thus interpretation, of current and likely future deterioration characteristics. The theme is illustrated with an example drawn from pitting corrosion.

2. Model development

The models of interest herein are those that can be applied directly to infrastructure rather than those built to mimic science fundamentals. In the latter area, there are serious

modelling efforts built on chemical and electrochemical processes (e.g. Sharland & Tasker, 1988; Shoesmith, 2003). This work is of fundamental importance but it has little direct application for many practical purposes. Moreover, there is usually only a tenuous link between corrosion in the laboratory and in the real world, as noted many times (Potter, 1972; Romanoff, 1962; US-ONR, 2007).

In the practical domain, a variety of empirical models for the progression of corrosion of mild and structural steels have been proposed. Largely, they are based on assumed corrosion growth curves. Because they are empirical, they seldom replicate actual field data particularly well, particularly in the case of longer-term exposures. The statistics extracted from such data often show very high levels of uncertainty, with the coefficient of variation exceeding the mean values. A brief review of such models particularly with application to shipping and offshore structures is available (Melchers, 2008a, 2009).

The most common model is the power law:

$$c(t) = At^B, \quad (1)$$

where $c(t)$ is corrosion as a function of time t and A and B are constants obtained from fitting it to the available data. Equation (1) was derived originally by Tammann (1923) from an idealistic model of the diffusion of oxygen through rust layers and a number of major assumptions and some mathematical simplifications. These have been reconsidered more recently (Melchers, 2003a).

Equation (1) has a long history of application particularly in the atmospheric corrosion literature. However, most attempts to use Equation (1) show high levels of uncertainty, and when attempts have been made to also account for climatic influences, the result usually is low confidence levels or poor correlation coefficients (Dean & Reiser 2002; Feliu, Morcillo, & Feliu, 1993a,

1993b; Morcillo, Simancas, & Feliu, 1995; Tidblad, Mikailov, & Kucera, 2000). Most likely this is because the influencing factors have been simplified or surrogates have been used for parameters that cannot be measured sufficiently easily. Mostly, all possible parameters have been included in the correlation studies, with little discrimination. Another reason appears to be that there is still insufficient understanding of the fundamental processes, although progress is being made. In addition, the correlation studies are based, as usual, on assumed linear correlation, although this is perhaps highly likely. While non-linear correlation could be employed, it does require at least knowledge of the general form of the underlying functions, even if only simplified functions are used in calibration.

A different approach altogether is to build a mathematical corrosion model based on known theory, including physical, electrochemical, chemistry and, in some cases, microbiological fundamentals. Such a model can be compared with actual observational data and calibrated to that data. This must allow for some degree of uncertainty associated with data and with observations. Thus, rather than letting the data dominate the form of the model, the approach is to construct the model based on reasonable expectations and seek to ascertain the extent to which the data can fit the prior model – in other words: ‘is the data sufficiently consistent with the model?’ Evidently, this approach is similar philosophically to the Bayesian theory for statistics (Ang & Tang, 1975) and it implies that the test for model suitability is whether it is possible to disprove the model. If this is the case, the choices are to refine the model or abandon it. This process may be repeated until a model of sufficient acceptability is obtained.

Because uncertainty must be considered in developing a suitable model for corrosion, an appropriate formulation is a probabilistic one (Melchers, 2003b). Thus, let corrosion loss $c(t, \mathbf{E})$ be a function of exposure period t and a vector $\mathbf{E}$ containing as elements environmental influences and material properties. In this case, a general formulation can be stated as:

$$c(t, \mathbf{E}) = b(t, \mathbf{E}) \cdot f(t, \mathbf{E}) + \varepsilon(t, \mathbf{E}), \quad (2)$$

where $f(t, \mathbf{E})$ is the mean-value function for corrosion loss, $\varepsilon(t, \mathbf{E})$ is a zero-mean error function and $b(t, \mathbf{E})$ is a bias function, all as functions of t and $\mathbf{E}$. From Equation (2), it follows immediately that if $f(t, \mathbf{E})$ is a poor choice the error term, $\varepsilon(t, \mathbf{E})$ will be large because the relationship between model and data will be poor. It also follows that effort in model development should primarily be spent on developing a good quality function $f(t, \mathbf{E})$. The next section considers this for the corrosion of steel in marine environments.

3. Model for marine corrosion

A model based on much observation of corrosion trends for a wide variety of comparable immersion corrosion sites is shown in Figure 2 (Melchers, 2003a; Melchers & Jeffrey, 2008; Melchers & Wells, 2006). The fundamental concept for the model is that the rate of corrosion at any one time is controlled by one or more of a number of possible diffusion processes. In that sense, it borrows directly from Tammann (1923) but does not assume there are no changes in the relative contributions of these various diffusion processes. In its simplest form, the model consists of a sequence of phases, each assumed to be controlled by a dominant or rate-controlling process.

In Figure 2, the first phase (0) consists of a complex mix of processes involving oxidation of the base metal, colonisation of the metal surface by biofilm and development of microbial activity within the biofilm. As this phase is quite short (days), it may be neglected for engineering purposes – indeed, it did not appear in the original model formulation (Melchers, 2003a). Phase 1 represents a relatively high rate of corrosion limited by so-called ‘concentration control’. In this mechanism, the rate of corrosion is limited by the rate at which oxygen can diffuse out of the surrounding (sea) water (or moisture layers).

This is a function of local water velocity and water temperature. It does not last very long because as the metal corrodes, some of the rust adheres to the metal and starts to inhibit the diffusion process. This develops into phase 2, where the rate of corrosion is controlled by the diffusion of oxygen through the rust layers. As these increase in thickness, the diffusion rate declines, and thus, the corrosion rate also declines. This is analogous to the model first proposed by Tammann (1923) and can be represented mathematically, after some important simplifications, as Equation (1) (Melchers, 2003a). Given sufficient time and build-up of rust products, the rate of oxygen diffusion to the corroding metal surface decreases, and by the end of phase 2, localised anoxic regions develop on the corroding surface.

As seen in Figure 2, at the end of phase 2, there is a considerable and relatively sudden increase in the instantaneous corrosion rate. This is the beginning of phase 3. Because of the anoxic conditions, it is possible, in principle, for anaerobic bacteria to be active during phase 3 and there is evidence to support this (Jeffrey & Melchers, 2003). Eventually, phase 3 shows a decline in the instantaneous rate of corrosion as further rusts develop and others are transformed to rusts with lower levels of permeability. The result is that corrosion eventually declines to an almost constant corrosion rate, represented by phase 4 of the model.

A specific feature of the model of Figure 2 is that it allows for the possibility of bacterial activity in the corrosion process. This possibility has long been

Table 1. Environmental factors and their effects on marine immersion corrosion.

Environmental factors	Importance
Bacteria	Can be high throughout
Biofouling (marine growth)	Mainly affects phase 1
Nutrients	Increases effect of bacteria and biofouling
Temperature	Important as it affects rates of kinetic reactions, of diffusion and of bacterial metabolism throughout
Oxygen concentration	Affects mainly phases 1 and 2
pH of environment	Affects mainly phase 1, i.e. before corrosion products build-up
Carbon dioxide concentration	Not significant
Salinity	Affects model throughout but generally the practical effect is low. Its effect is moderated by carbonate concentration
Carbonate concentration	Builds less permeable rusts and thus reduces corrosion throughout
Pollutants	Little effect unless high
Pressure	Little effect
Stress	Higher stresses cause loss of protective rusts
Fatigue loading and stress	Ditto
Suspended solids	Little effect unless erosion involved
Wave action	Important if high
Water velocity	Important if high

recognised for steel corrosion in certain natural environments (Beijerinck, 1895; Little & Lee, 2007) but had not been considered in any model. The bacteria recognised as the main serious influence on the corrosion of steel (and some other metals) are the obligatory anaerobic sulphate reducing bacteria (SRB) (Little & Lee, 2007). There are several species now known to be involved. This in itself is of little direct import to engineering – what is important is not the bacteria actually present but rather what they do and to what they respond. Bacteria require energy, nutrients and an appropriate environment. They also have to be at the location where they can damage. For the corrosion of steel in seawaters or in marine atmospheres, normally all are the requirements are met or provided except perhaps for the availability of the nutrient nitrate (Carlucci, 1974). For this reason, Figure 2 shows the effect of bacteria by the green curves marked ‘increasing nutrient levels’ in phases 3 and 4. It is also possible to have microbiologically influenced corrosion in phases 0–2. This arises from the development of anoxic conditions within biofilms (phases 0–2), a matter that has received much research attention in the microbiological literature (Little & Lee, 2007). In this case too, SRB are the bacteria most often implicated. These influence corrosion through the production of the metabolite H_2S . This has an aggressive effect on steel

causing closely spaced pitting and producing FeS which is a black, soft, slimy corrosion product easily removed to reveal bright steel underneath. When exposed to air, the metal surface quickly oxidises to produce conventional red-brown oxidation products. Other bacteria may be involved also, including iron oxidisers, iron reducers and manganese bacteria with similar characteristics (Little & Lee, 2007).

The electro-chemical reactions that make up and that control the corrosion processes in the phases of the model of Figure 2 need not be considered here, except to note that they differ significantly between phases 0–2 and phases 3 and 4. The former are controlled essentially by oxygen rich conditions (Melchers, 2003a), while the latter occur primarily under, perhaps localised, oxygen poor conditions. The corrosion process for the latter is not yet completely understood (Melchers, 2012) but involves pitting under autocatalytic conditions (Shrier, 1994; Wranglen, 1974). However, these details are not central to the present discussion.

Apart from bacteria, other factors known to influence corrosion in seawater include those shown in Table 1. Of these, water temperature has a strong influence on the model. This is shown schematically in Figure 2. It affects the kinetics of chemical reactions, the rates of diffusion involved in governing the rate of corrosion, the concentration of dissolved oxygen (DO) and the rate of bacterial metabolism. In addition to the factors in Table 1, metal composition, surface roughness and geometry and orientation and the effect of applied stress can be important.

The bimodal model shown in Figure 2 has been calibrated to a range of data for natural coastal seawater where wave action and water velocity were low to moderate and for mild and for copper-bearing steels. The parameters r_0 , c_a , t_a , c_s and r_s shown in Figure 2 were derived from this work as functions of annual average seawater temperature (Melchers, 2003a; Melchers & Wells, 2006). As noted above, for structural reliability evaluation, the uncertainty about the model is of considerable interest. This aspect is contained in the terms b and ε in Equation (2). The traditional empirical corrosion literature has ignored it. Evaluating these two terms requires multiple samples for any one exposure time to estimate the mean and at least the standard deviation. Some preliminary information is now available (Melchers, 2003b) and more is being obtained in on-going research activities. Similarly, while the evaluation of the effect of some of the influencing factors shown in Table 1 has been given research attention, most remain for investigation.

4. Generalisation and comparison to data

For models to be accepted they must, ultimately, relate to reality. As noted, the model shown in Figure 2 and

Figure 3. Sample of long-term data showing that the corrosion process is not linear in the immersion, tidal and atmospheric zones.

described above has been calibrated to actual field data, including some long-term data. It also has been extended to weathering steels, to steels with elevated chromium contents and to fresh and brackish waters as well as to exposures in different atmospheric conditions. However, lack of sufficient data has delayed model calibration for these cases. Nevertheless, comparisons can be made with available data and their trends. In this regard, the most useful data are the observations extending over 16 years in the Panama Canal Zone (Forgeson, Southwell, & Alexander, 1960; Southwell, Forgeson, & Alexander, 1958). Considering only mild steel coupons, Figure 3 shows the trends under four different marine-related environments – immersion, mid-tide, marine coastal and 1.6 km inland from there. These trends have been interpreted from the data given in the original sources, although that was not always in the form shown in Figure 3. Trends with generally similar bimodal characteristics have been found applicable to data sets for various low alloy and chromium steels (Melchers & Jeffrey, 2008).

One important aspect seen in Figure 3 is that corrosion loss as a function of time cannot be expressed simply by a ‘corrosion rate’, which, in Figure 3, is a straight line through the origin. Depending on how a straight line was fitted to the data, use such a simplistic measure that either over- or underestimates actual corrosion losses by a very considerable amount at least somewhere within the 16 years. However, a simple representation of the trends in Figure 3 can be achieved, as described in the next section.

5. An engineering model

For conservative prediction of marine immersion corrosion, the model of Figure 2 may be simplified. For longer term corrosion, the details of transitional phases 2 and 3 may be of limited interest. Conversely, the early behaviour

Figure 4. Simplified (engineering) model for marine immersion corrosion loss. The effects of increased nutrient concentration and DO concentration are shown.

represented by phase 1 is likely to be of interest for the initial corrosion period. Hence, the model in Figure 2 can be simplified by ignoring the detail provided by phases 2 and 3, allowing the early corrosion loss to be represented by the initial corrosion rate r_0 with the total corrosion loss bounded from above by the long-term rate r_s and its axis intercept c_s . The model that represents these aspects is shown in Figure 4.

In Figure 4, the commencement of the long-term approximately steady-state corrosion in phase 4 is denoted by t_s with $t_s - t_a$ as obtained from limited data, around 1–1.5 years in duration (Melchers & Wells, 2006). The value of t_a depends on average seawater temperature T . This also applies to r_0 . Calibration to a wide collection of ‘at-sea’ field data (Melchers, 2003a) showed that they can be modelled as:

$$t_a = 6.61 \exp(-0.088T), \quad (3)$$

$$r_0 = 0.076 \exp(0.054T). \quad (4)$$

For the simplified model shown in Figure 4, the mean (expected) value of corrosion loss $c(t)$ now can be represented, with obvious notation, by:

$$c(t)|_E = \min [(r_0 \cdot t), (c_s + r_s \cdot t)]|_E, \quad (5)$$

where E represents the variables in Table 1 as well as any material factors. To apply Equation (5), it is necessary to have estimates for parameters c_s and r_s . As before, examination of extensive sets of data for immersion corrosion of low carbon steels in unpolluted seawaters (Melchers & Wells, 2006) has found that for carbon steels in the range $5^\circ\text{C} < T < 30^\circ\text{C}$, they can be represented by:

$$c_s = 0.141 - 0.00133 T \quad (6)$$

$$r_s = 0.039 \exp(0.0254 T) \text{ for carbon steels} \quad (7)$$

Figure 5. Variation of the parameter c_s for long-term corrosion as a function of T .

$$r_s = 0.0343 \exp(0.0476 T) \text{ for copper-bearing steels.} \quad (8)$$

These relationships are shown in Figures 5 and 6. They were all derived using the model of Figure 2 as a guide and using interpretations of data to construct corrosion loss – exposure period curves.

The fitting of the relations Equations (5)–(8) implies a degree of uncertainty in addition to uncertainty in the data itself and this should be reflected in uncertainty in the parameters r_0 , c_s and r_s . Uncertainty in the initial corrosion rate r_0 may be estimated from the same set of data used for calibration (Melchers, 2003b). This provided a standard deviation of about 0.03 over a range of seawater temperatures. Also, the bias factor b was found to be close to unity and therefore may be ignored. To obtain an estimate of the uncertainty in c_s the scatter in the data points for c_s about Equation (6) was analysed. This produced a standard deviation of $\sigma_{cs} \approx 0.019$ for both carbon and copper-bearing steels, irrespective of water temperature. A similar analysis for r_s showed that seawater temperature did need to be considered. The estimated values for the standard deviation σ_{rs} are shown in Figure 7 together with a best fit curve, assumed exponential (reflecting the variation of r_s with T).

6. Example

The simplified model in Figure 4 will now be applied to predict the immersion corrosion loss of structural mild steel likely to occur over a period of 10 years in the clean seawaters with estimated mean annual seawater temperature of 20°C. For this temperature, Figures 5–7 show that $r_s = 0.07$ mm/yr, $\sigma_{rs} = 0.009$ mm/y and $c_s = 0.11$ mm and also $\sigma_{cs} \approx 0.019$ mm. Assuming $t_a \approx 1.2$ years, it follows

Figure 6. Variation of the parameter r_s for long-term corrosion as a function of T .

that $t_a + t_s < 2.7$ years, which means that phase 4 behaviour governs at 10 years exposure and hence the second term of Equation (5) governs. It follows that the expected corrosion loss from one face of the metal at that time is:

$$c(t = 10) = 0.11 + (0.07)(10) = 0.84 \text{ mm} \quad (9)$$

with variance σ_c^2 given by:

$$\begin{aligned} \sigma_c^2 &= \sigma_{cs}^2 + (t)^2 \sigma_{rs}^2 = (0.11)^2 + (10)^2 (0.009)^2 \\ &= 0.02 \text{ mm}^2 \end{aligned} \quad (10)$$

from which $\sigma_c(10) = 0.14$ mm. Also, the long term expected corrosion rate after 10 years exposure is simply

Figure 7. Estimated standard deviation of r_s (i.e. σ_{rs}) as a function of average seawater temperature.

Figure 8. Corrosion loss function for longer term corrosion showing expected value at 10 years and the uncertainty about this value. Also shown is the increasing uncertainty from $t = 0$.

given by $r_s = 0.07$ mm/y with standard deviation $\sigma_{rs} = 0.009$ mm/y.

These results are sketched in Figure 8, indicating the expected corrosion loss at 10 years (0.84 mm) as well as the anticipated uncertainty about this value, given by a standard deviation of ± 0.14 mm. As is usual in uncertainty estimates, if there is no additional information about the potential probability distributions to be attached to the variable, the probability distribution is taken as Normal. Then, it is determined readily that the expected corrosion loss at 10 years exposure will be less than $0.84 + (1.56) \cdot (0.128) = 1.02$ mm with 90% confidence and, similarly, less than 1.07 mm with 95% confidence.

For short corrosion periods, less than $t_a + t_s$, corrosion will not be governed by phase 4 behaviour and is instead, best described by phase 1, 2 or 3 (Figure 2). For example, for an exposure period of 0.8 years, a conservative estimate is to assume phase 1 governs and to use first term of Equation (5) as the governing condition. The estimated expected value of corrosion is:

$$c(0.8) = r_0 \cdot (0.8) = (0.22)(0.8) = 0.176 \text{ mm} \quad (11)$$

with a standard deviation:

$$\sigma_{r_0} = [(0.8)^2 \cdot (0.03)^2]^{1/2} = 0.024 \text{ mm} \quad (12)$$

for which the 90% and 95% values are 1.79 and 1.8 mm, respectively.

7. Discussion

The above exposition has provided a logical model consistent with basic notions in corrosion science and consistent with data and data trends from actual field observations. In this sense, it varies significantly from electrochemical laboratory based testing that at best provides an estimate of r_0 and then only so under the conditions of the laboratory. There is no doubt that laboratory test conditions can be very carefully specified and controlled while field observations are essentially

uncontrolled and the investigator has to make the best of what is available and what can be measured under field conditions (Lee, Ray, & Little, 2010). The investigation method of choice ultimately depends on the purpose. For generating scientific understanding and for exposing relationships particularly at the nano- and microscale, laboratory testing undoubtedly is the appropriate choice.

However, for obtaining relationships that are likely to be used in engineering applications, the approach outlined herein appears to be a more useful approach. This does mean, however, for the field data based models to have an acceptable degree of validity they must be based on a good understanding of corrosion fundamentals; otherwise, they are merely empirical constructs with no claim to validity and to have prediction capability. As noted, such an approach relies on calibration to real-world observations. This implies recognition that some level of uncertainty always will remain. In turn, this means that a probabilistic framework is essential, and this in turn makes demands for ascertaining at least second order statistics, a matter very uncommon in the conventional corrosion experimental world, with one important exception.

Only in the treatment of pit depth has probability theory been pursued in the corrosion literature. It has done so by assuming that the depths of the set of deepest pits that have formed at any point in time on a metal surface as a result of corrosion can be represented by the Gumbel Extreme Value distribution (Galambos, 1987). There is a long history in the corrosion literature going back to 1956 (Aziz, 1956), and in the extreme value literature, the use of the Gumbel distribution to represent the probability distribution of the deepest pits was seen as a classical application (Galambos, 1987).

Recently, however, it has been argued that this makes the unjustified assumption that the population of pits is homogeneous, whereas the empirical evidence would indicate it is not. This may be seen from a plot of the progression of the deepest and a set of deepest pits (Figure 9). It shows that in general terms the trends follow the bimodal trend seen for corrosion loss (Figure 2) with different overall rate controlling mechanisms before and

Figure 9. Plot of maximum pit depth as a function of exposure period and also the trend for the mean of the six deepest pits measured on 18 replicate surfaces at each recovery time, at 1, 2, 3 and 4 years approximately (Melchers, 2008b).

after about one year of exposure. In simple terms, there are at least two different statistical populations involved. However, most investigators have considered only relatively short exposure periods and for these it may be reasonable to assume homogeneity. Even in this case, close inspection of the development of pitting shows that it is characterised by various discontinuities in development of pit depth (Jeffrey & Melchers, 2007). Again, a sound understanding of the underlying processes is essential for the modelling process to represent reality and thus to be useful for data interpretation and for extrapolation.

The bimodal feature seen in Figures 2 and 9 is not confined to seawater exposures. It has been observed also for exposure of steel in fresh water and in distilled water. Consequently, the characteristics of the water and the possibility of bacterial involvement cannot be the underlying reason for the bimodal characteristic (Melchers, 2012). In turn, this means that the bi-modal behaviour must be purely electrochemical. It has been proposed (Melchers, 2012) that the electrochemical mechanisms most likely involved occur in the early part of phase 3 and are similar to those in the autocatalytic, low pH process for crevice and pitting corrosion first proposed by Wranglen (1974). This process requires an aggressive ion, for steel usually either chlorides or sulphides or both, even though neither need play a direct role in the chemical reactions. They provide the potential drop that governs the depth of the crevice or pit (Turnbull, 1994). Although Wranglen proposed this model many years ago and there is computational support (e.g. Sharland & Tasker, 1988), its application as a possible explanation for the development of the bi-modal model (Figure 4) is recent (Melchers, 2012).

8. Conclusions

The development of models for the long-term corrosion of structural steel exposed to seawater and marine environments facilitates prediction of longer term corrosion and pitting. Increasingly, this is desirable and necessary for the management of older infrastructure and for the design of new infrastructure to ensure satisfactory safe and serviceable lives. Models based on corrosion fundamentals and calibrated to field data permit more informed interpretation of new observations and also provide a sound basis for extrapolation. They are therefore much more powerful than empirical models based on data alone. However, uncertainty must be considered and this was illustrated with a simple example.

Acknowledgements

The continued financial support of the Australian Research Council through two successive Australian Professorial Fellowships and various Discovery Grants is acknowledged with gratitude.

References

- Ang, A.H.-S., & Tang, W.H. (1975). *Probabilistic concepts in engineering planning and design: Basic principles* (Vol. 1). New York, NY: Wiley.
- Aziz, P.M. (1956). Application of the statistical theory of extreme values to the analysis of maximum pit depth data for aluminum. *Corrosion*, 12, 495t–506t.
- Beijerinck, M.W. (1895). Über *Spirillum desulfuricans* als Ursache von Sulfat-reduktion [The species *desulfuricans* as cause of sulfate reduction]. *Zentralblatt für Bakteriologie, Parasitenkunde, Infektionskrankheiten und Hygiene, Section I*, 1, 104–114.
- Carlucci, A.F. (1974). Nutrients and microbial response to nutrients in seawater. In R.R. Colwell & R.Y. Morita (Eds.), *Effect of the ocean environment on microbial activities* (pp. 245–248). Baltimore, MD: University Park Press.
- Committee. (2006). Condition assessment of aged ships, Committee V.6 Report, International Ship Structures Committee. *Ships and Offshore Structures*, 2, 261–271.
- Dean, S.W., & Reiser, D.B. (2002). Analysis of long-term atmospheric corrosion results from ISO CORRAG program. In H. Townsend (Ed.), *Outdoor atmospheric corrosion*, STP 1421 (pp. 3–18). West Conshohocken, PA: American Society for Testing and Materials.
- Feliu, S., Morcillo, M., & Feliu, S. Jr (1993a). The prediction of atmospheric corrosion from meteorological and pollution parameters: I. Annual corrosion. *Corrosion Science*, 34, 403–414.
- Feliu, S., Morcillo, M., & Feliu, S. Jr (1993b). The prediction of atmospheric corrosion from meteorological and pollution parameters: II. Long-term forecasts. *Corrosion Science*, 34, 415–422.
- Forgeson, B.W., Southwell, C.R., & Alexander, A.L. (1960). Corrosion of metals in tropical environments. Part 3: Underwater corrosion of ten structural steels. *Corrosion*, 16, 105t–114t.
- Galambos, J. (1987). *The asymptotic theory of extreme order statistics* (2nd ed.). Malabar, FL: Krieger.

- Gudze, M.T., & Melchers, R.E. (2008). Operational based corrosion analysis in naval ships. *Corrosion Science*, 50, 3296–3307.
- Jeffrey, R., & Melchers, R.E. (2003). Bacteriological influence in the development of iron sulphide species in marine immersion environments. *Corrosion Science*, 45, 693–714.
- Jeffrey, R., & Melchers, R.E. (2007). The changing topography of corroding mild steel surfaces in seawater. *Corrosion Science*, 49, 2270–2288.
- Lee, J.S., Ray, R.I., & Little, B.J. (2010). The influence of experimental conditions on the outcome of laboratory investigations using natural coastal seawaters. *Corrosion*, 66, 105001-1–105001-6.
- Little, B.J., & Lee, J.S. (2007). *Microbiologically induced corrosion*. New York, NY: Wiley.
- Melchers, R.E. (1999). *Structural reliability analysis and prediction*. Chichester: Wiley.
- Melchers, R.E. (2003a). Mathematical modelling of the diffusion controlled phase in marine immersion corrosion of mild steel. *Corrosion Science*, 45, 923–940.
- Melchers, R.E. (2003b). Modeling of marine immersion corrosion for mild and low alloy steels. Part 2: Uncertainty estimation. *Corrosion*, 59, 335–344.
- Melchers, R.E. (2008a). Development of new applied models for steel corrosion in marine applications including shipping. *Ships and Offshore Structures*, 3, 135–144.
- Melchers, R.E. (2008b). Extreme value statistics and long-term marine pitting corrosion of steel. *Probabilistic Engineering Mechanics*, 23, 482–488.
- Melchers, R.E. (2009). Experiments, science and intuition in the development of models for the corrosion of infrastructure. In *Corrosion and Protection 2009: The Management of Infrastructure Deterioration: Conference Proceedings*, Coffs Harbour, NSW, Australia, 15–18 November 2009. Melbourne: Australasian Corrosion Association.
- Melchers, R.E. (2012). The relative influence of microbiological and abiotic processes in modelling longer-term marine corrosion of steel. *Eurocorr2012 Proceedings*, Istanbul..
- Melchers, R.E., & Jeffrey, R. (2008). Modeling of long-term corrosion loss and pitting for chromium-bearing and stainless steels in seawater. *Corrosion*, 64, 143–154.
- Melchers, R.E., & Wells, P.A. (2006). Models for the anaerobic phases of marine immersion corrosion. *Corrosion Science*, 48, 1791–1811.
- Morcillo, M., Simancas, J., & Feliu, S. (1995). Long-term atmospheric corrosion in Spain: Results after 13–16 years of exposure and comparison with worldwide data. In W.W. Kirk & H.H. Lawson (Eds.), *Atmospheric Corrosion*, ASTM STP 1239. West Conshohocken, PA: American society for Testing and Materials.
- Paik, J.K. & Melchers, R.E. (Eds.). (2008). *Condition assessment of aged structures*. Cambridge: Woodhead.
- Potter, E.G. (1972). The corrosion scene in Australia. *Australasian Corrosion Engineering*, 16, 21–29.
- Romanoff, M. (1962). *Corrosion of steel pilings in soil*, National Bureau of Standards Monograph 58. Washington, DC: U.S. Department of Commerce.
- Sharland, S.M., & Tasker, P.W. (1988). A mathematical model of crevice and pitting corrosion. I: The physical model. *Corrosion Science*, 28, 603–620.
- Shoesmith, D.W. (2003). Development of corrosion models based on electrochemical measurements. In R.G. Kelly, J.R. Scully, D.W. Shoesmith, & R.G. Buchheit (Eds.), *Electrochemical techniques in corrosion science and engineering*. New York, NY: Marcel Dekker.
- Shrier, L.L. (1994). Localised corrosion. In L.L. Shrier, R.A. Jarman, & G.T. Burstein (Eds.), *Corrosion* (3rd ed., Vol. 1) (pp. 1:151–1:212). Oxford: Butterworth-Heinemann.
- Southwell, C.R., Forgeson, B.W., & Alexander, A.L. (1958). Corrosion of metals in tropical environments. Part 2: Atmospheric corrosion of ten structural steels. *Corrosion*, 14, 53–59.
- Tammann, G. (1923). *Lehrbuch der Metallographie* (2nd ed.). Leipzig: Leopold Voss.
- Tidblad, J., Mikailov, A.A., & Kucera, V. (2000). Application of a model for prediction of atmospheric corrosion in tropical environments. In S.W. Dean, G.H.D. Delgadillo, & J.B. Bushman (Eds.), *Marine corrosion in tropical environments*, ASTM STP 1399 (pp. 18–32). West Conshohocken, PA: American society for Testing and Materials.
- Turnbull, A. (1994). Mathematical modelling of localized corrosion. In K.R. Trethewey & P.R. Roberge (Eds.), *Modelling aqueous corrosion: From individual pits to system management*, NATO ASI series E. (Vol. 266) (pp. 63–79). Dordrecht: Kluwer.
- US-ONR (2007). *Second World Congress on Corrosion in the Military*, Naples, September. London: US Office of Naval Research (Global).
- Wranglen, G. (1974). Pitting and sulphide inclusions in steel. *Corrosion Science*, 14, 331–349.