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The critical involvement of anaerobic bacterial activity in modelling the corrosion behaviour of mild steel in marine environments

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ABSTRACT

The modelling of both short- and long-term corrosion loss and maximum pit depth is increasingly of interest to engineers and others interested in predicting the remaining life of coastal and ocean infrastructure. Traditional models are demonstrably of poor quality. A more refined modelling approach applicable both to corrosion loss and to pitting of mild steel in marine environments is described. A crucial aspect is that explicit consideration is given to the influence of microbial activity. The model is unique in that it considers the governing corrosion process to change with increased exposure time. The rationale for this approach and some of the key findings are described. It is supported by observations of the corrosion response to changes in metal alloying and to water pollution effects. The model also permits more rational explanations to be offered for the effects of water velocity, depth of immersion and seawater salinity. Recently the effect of anaerobic bacteria on very early corrosion has been re-examined and an explanation offered in terms of the influence of water pollution on the initial corrosion rate. Applications to pitting corrosion of mild steel has led to new interpretations of pit data and new interpretations for the probability distributions associated with maximum probable pit depth. The model has been calibrated using an extensive re-examination of literature data and extensive use of specially commissioned field tests.

1. Introduction

The modelling of both short- and long-term corrosion loss and maximum pit depth is increasingly of interest to engineers and others interested in predicting the remaining life of coastal and ocean infrastructure. Models for corrosion loss and pit depth have a number of applications, including (i) allowing engineers and others to interpret field observations to assess the significance of the corrosion currently observed, (ii) to estimate how much more corrosion can be expected in the future, and (iii) to help assess what is a reasonable or acceptable degree of corrosion. These questions invariably require the prediction of likely future technical scenarios, and this invariably involves models, preferably those that have a high degree of prediction capability and transportability. Many traditional 'models' in the corrosion literature fail on both counts. Moreover, few are capable of long-term prediction as typically required for infrastructure applications. This paper describes recent progress in developing a model for corrosion loss and for maximum pit depth based on corrosion fundamentals and, importantly, including the critical role of microbiological activity. An integrated approach of this type appears not to have been developed previously.

Discussion herein is limited to structural (mild) steels exposed to marine (seawater) environments. It is assumed that protective systems such as such as protective coatings (paints), sacrificial coatings (galvanizing) and cathodic protection are absent or have already failed. This is typical for structures subject to poor maintenance regimes.

For infrastructure two matters are of particular interest: corrosion loss and maximum pit depth. The first has a strong influence on structural strength and the second is critical in containment capability. Areas of application include ships, offshore and coastal structures, pipelines and nuclear containers in saline groundwaters.

The potential involvement of bacteria in corrosion processes has long been recognized in the corrosion literature for short-term corrosion and for corrosion initiation [1] and independently for long-term marine immersion corrosion [2]. Detrimental bacteria have been noted in field observations, for a variety of materials including structural steels [3] and stainless steels [4,5]. However, what has been lacking is a proper framework for connecting the involvement of bacteria (often measured simply by the numbers present) with the degree of corrosion loss and pitting depth, with period of exposure and with environmental conditions. Simply noting that bacteria are present and that corrosion may have been influenced by microbial action is neither helpful nor convincing.

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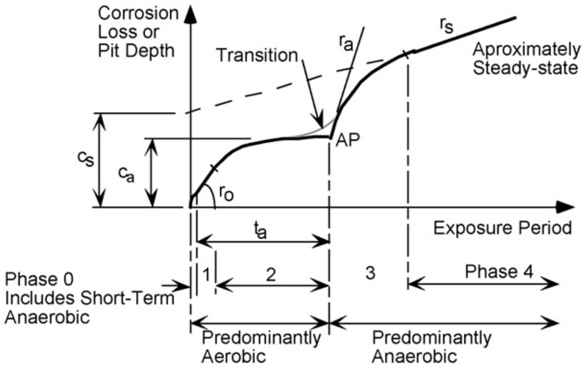

Fig. 1. Corrosion loss – exposure time model showing each of the phases and the parameters used to define them.

2. Models for corrosion loss

Models for corrosion loss are generally acknowledged to have commenced with Tammann [6] who solved the mathematics for the diffusion of oxygen through the tarnish layers formed on copper. Refinement of the mathematics followed [7,8] although this usually is simplified to a corrosion or pit depth $c(t)$ growth law of the form

$$c(t) = At^B \tag{1}$$

where t is time and A and B are constants. This expression is used in at least one very refined model for pit initiation and early pit growth [9]. Expression (1) also forms the basis for much modelling of long-term atmospheric corrosion loss (e.g. [10]). This work is based on the assumption that the oxidation process commences immediately on first exposure and lasts indefinitely. However, many analyses have shown that the data does not always fit the model very well but this is either ignored or dismissed as due to data inaccuracies. Various other models of a more empirical nature, in some cases with a long-term steady-state corrosion loss rate, and in other cases including an empirical allowance for the deterioration time of protective coatings, have been proposed [11–14]. Mostly these models are calibrated to relatively short-term data (typically 2–4 years) or to aggregated data from a wide variety of sources without discrimination. As a result they have wide variability and poor predictive capability.

In 1997, Melchers [15] postulated that the corrosion process changes with time and could be represented by a number of sequential phases. The model, since refined, is shown in Fig. 1 [16]. It includes both metal oxidation (in the aerobic phases 1 and 2) and bacterial activity (in the anaerobic phases 3 and 4) (Table 1). Metal oxidation in phases 1 and 2 follows the conventional principles of electrochemistry [8] and need not be discussed here. Importantly, both phases are rate controlled not by the kinetics of the oxidation process but by the rate of oxygen diffusion. As summarized in Table 1, for phase 1 this is then the rate at which oxygen can diffuse out of the seawater (or moisture layer) through the as yet thin corrosion product layer to the corroding surface. For phase 2 the gradually increasing thickness of the rust layers provides the rate control for oxygen diffusion, following the classical theories but with the initial conditions properly defined [17].

Phase 4 of the model was built on the interpretation by Southwell et al. [2] of long-term (16 years) data for corrosion observations in the Panama Canal Zone. In a paper largely ignored in the corrosion literature, these authors concluded that anaerobic bacteria and in particular the sulphate-reducing bacteria (SRB) are the main agents for long-term corrosion. Their work has been extended by recognizing there must be a transition from aerobic to anaerobic corrosion behaviour and that there is a relative short period of elevated bacterial activity resulting in temporary higher corrosion rates (phase 3). The activity of SRB can be represented by the rate of bacterial metabolism. This results in bacterial metabolites, of which hydrogen sulphide (H_2S) is the principal component. Its electrochemistry is well-known. The corrosive effect of H_2S also is well-known. It differs from that of oxygen. As will be seen, this has important implications for testing the model and for its calibration. Importantly, the rate of metabolism of the SRB is controlled by the rate of availability of nutrients critical for the metabolic process. In seawater the critical nutrient usually is nitrogen in the form of nitrates, nitrites and ammonia [19].

Mathematical descriptions (models) for phases 1 and 2 and for 3 and 4 have been derived using fundamental concepts of oxygen and nutrient diffusion respectively and calibrated to in-situ natural seawater observations of corrosion loss [17–19]. For practical applications the diffusion equations need not be solved – only the general shape of the curve for each phase is of interest and these have been parameterised as shown in Fig. 1. The model in Fig. 1 is an idealization. In practice not all points on a corroding surface will experience the same phenomenon and hence the transitions from one controlling process (phase) to another are likely to be gradual.

The model parameters have been calibrated to in-situ corrosion loss data as a function of mean seawater temperature, for essentially unpolluted coastal seawaters and for a wide variety of geographic locations. The data was extracted from the literature and supplemented by data (and subjective estimates) for environmental conditions [16]. Estimates were made also of uncertainty of the model relative to the data [20]. It is found that typically the variance increased, in some cases substantially, once the corrosion process was governed by bacterial activity, that is, at the end of phase 2 and into phases 3 and 4. Generally similar findings were obtained for pitting corrosion [21].

3. Evidence for involvement of bacterial activity

3.1. *Early corrosion (phase 0)*

Laboratory observations have provided convincing evidence of the potential of SRB and other bacteria to be involved in the pitting

Table 1
Summary description of the phases of the model (Fig. 1)

Phase	Corrosion process
0	On immersion steel surface is colonized by biofilm, bacteria and marine organisms and subject to a complex mix of localized influences. Bacterial metabolites may influence early corrosion if nutrient supply is elevated.
1	Oxidation process controlled by rate of arrival of oxygen at the metal surface from the surrounding seawater (‘oxygen concentration’ control). Rust layers are still very thin. The resulting corrosion loss may be modelled, closely, as a linear function
2	Build-up of corrosion products (rust) increasingly retards the rate of oxygen supply to the corroding surface (‘oxygen diffusion’ control). Increasing thickness of the rust layer reduces the capability for oxygen to reach the corroding surface, thereby allowing localized anaerobic conditions to develop at AP
3	Sulphate-reducing bacteria (SRB) flourish under appropriate nutrient supply conditions. The rate of corrosion now depends on rate of bacterial metabolism. This depends on rate of supply of nutrients, including those stored in the rust layers
4	Metabolism of sulphate-reducing bacteria (SRB) depends on rate of nutrient supply. Allowing also for the slow loss of rust layer through erosion and wear this phase may be modelled as near-steady-state and almost linear