



# Long-term immersion corrosion of steels in seawaters with elevated nutrient concentration



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## ABSTRACT

Data from a variety of field exposure programs is used to quantify the effect of concentration of dissolved inorganic nitrogen (DIN) on long-term seawater immersion corrosion loss of structural steels. A linear correlation model that asymptotes the long-term part of the previously proposed bi-modal corrosion loss model is used. It allows for average seawater temperature. Model parameters and their variability are determined and reported. The model permits prediction of long-term corrosion loss in nutrient polluted waters of known average temperature. An example shows that anthropological pollution of seawater potentially is a major hazard for corrosion of steel infrastructure.

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## 1. Introduction

A previous paper [1] considered the ratio of the corrosion loss of steel piling immediately below the low tide level relative to the corrosion loss in the immersion zone. It, and a subsequent paper [2], showed that this ratio is positively correlated with the annual average concentration of dissolved inorganic nitrogen (DIN) in the local bulk seawater. However, the actual magnitude of corrosion loss was not established. The present paper deals with estimating the magnitude of the corrosion loss in immersion conditions under elevated DIN concentrations. Specifically, a quantified relationship is developed between immersion corrosion loss and the average DIN in the seawater local to the steel of interest. Such a relationship has not been developed previously.

Structural steel is used widely for major infrastructure in or around seawater harbours, for shipping and for offshore structures. Protection using coatings or cathodic protection systems or both can be effective if properly maintained. However, some infrastructure is unsuited to such protective measures and reliance usually is then placed on a sacrificial corrosion allowance. For example, corrosion allowances in ships [3] typically are given in terms of a corrosion rate, such as 0.1–0.5 mm/y, implying that corrosion loss is a linear function of time, commencing at the origin. However, a variety of data show that corrosion loss for steel in marine exposure conditions is not a simple linear function of time [4,5]. It also is a function of water temperature and may be subject to the additional effect of microbiologically influenced corrosion (MIC). The latter is known to be a function of the nutrients, and in particular

DIN, present in seawater [6]. This has been demonstrated in laboratory experiments [7] and, more recently in both short term and long-term field observations [8,9]. These works did not, however, develop quantitative relationships between immersion corrosion loss and the seawater DIN concentration in the immediate vicinity of the corroding steel.

Considerable research effort has focussed on identification and understanding the behaviour of the many microorganisms potentially involved in the microbiologically influenced corrosion (MIC) of steel in seawater [6]. In brief, the species traditionally associated with corrosion of steel in seawater are the obligatory anaerobic sulphate reducing bacteria (SRB) for which the causative agent for MIC has been considered the metabolic product  $H_2S$  [10]. However, many other species, including archaea, have been implicated in causing MIC [11] and the list continues to grow [12,13]. Irrespective of the precise species involved, microbiological activity can influence corrosion only if the microorganisms are in appropriate environmental conditions and have sufficiently high rates of supply of energy and of necessary nutrients [6]. In the corrosion process energy is available directly from the electron flow associated with electrochemical and chemical reaction kinetics. In natural seawater most nutrients, such as organic carbon, sulphates and phosphates are readily available and in steel corrosion the nutrient usually limiting microbiological activity, iron, is provided by the corrosion process as  $Fe^{2+}$  [6].

Rather than focussing directly on the microorganisms and their interaction with and influence on the corrosion processes, a more practical approach is to consider the relationship between the availability of DIN for microbiological activity and the severity of the resulting corrosion. This approach by-passes detailed consideration

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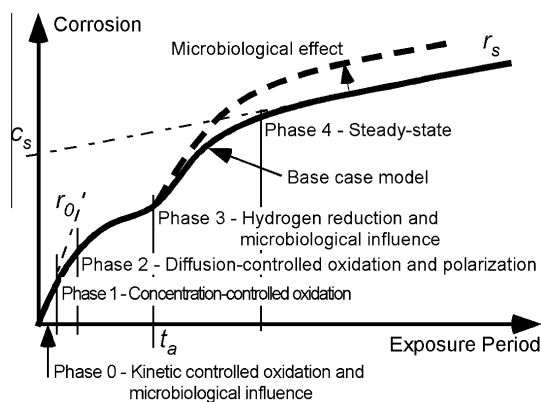
of the complex issues associated with microbiology. Instead it considers input–output correlation between nutrient concentration and corrosion loss or corrosion behaviour. This approach has been applied successfully for estimating the effect of DIN concentration on the accelerated low water corrosion (ALWC) of steel piling in seawater harbours [1,2]. It is applied also for the analysis described below. It is noted in passing that even in heavily polluted waters the concentration of DIN is much too low to have a direct effect on the purely electro-chemical corrosion processes, that is through changing the properties of the electrolyte (seawater).

In principle, a relationship between the long-term marine immersion corrosion loss of steel, the DIN concentration in the bulk seawater, the average water temperature and the length of the exposure period could be developed empirically using only field observations. However, a more rational approach is to employ also knowledge gained from earlier studies about the expected progression of corrosion with exposure time. The next section outlines this earlier work, including the basic corrosion loss – exposure time model and its linearised simplification. This is then used to interpret available data and to evaluate the parameters for the model as functions both of average DIN and of annual mean water temperature.

## 2. Corrosion loss function

A non-linear model for the progression of uniform or general corrosion through a series of sequential phases was proposed earlier and calibrated to available long-term data that took into account the significant influence of seawater temperature [4]. The theoretical basis for the main parts of the model, and the associated mathematical expressions, has been described [14]. The model has been refined and extended to deal with dissolved oxygen concentration, seawater velocity and the influence of steel composition and it has been shown to apply also to tidal and marine coastal atmospheric exposures [15]. A schematic summary of the principal parts of the model is shown in Fig. 1. The solid line shows the bi-modal corrosion trend under abiotic conditions and the broken line the effect of MIC on longer-term corrosion loss.

It is well-known MIC can contribute to corrosion from the beginning of exposure as shown both in laboratory and field studies [7,8] but for the present purposes only the effect on longer-term corrosion (phases 3 and 4) is of interest. The mechanism most likely to be rate-controlling for longer-term corrosion is diffusion of nutrients through the rust layers [14]. As a first approximation this may be modelled as Fickian diffusion, governed by diffusivity

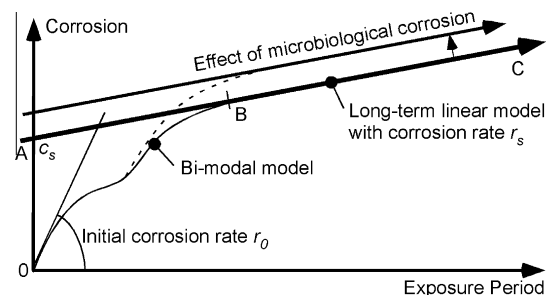


**Fig. 1.** Schematic non-linear (bi-modal) model (solid trend line) for the progression of (uniform) corrosion loss with time showing the influence of some of the major parameters involved, including the influence of nutrients (shown as microbiological effect, broken line) on long-term corrosion. On the horizontal time scale  $t_a$  is about 1 year for waters at 20 °C average and about 3 years for waters at 10 °C average. Phases 0–4 have been described in the literature [4,15].

of the rusts and by the concentration of nutrients in the bulk water assuming they are fully consumed within the rusts. As a result of the enhanced rate of microbiological processes a greater rate of rust production can be expected (i.e. due to MIC) and overall thicker, more developed rusts can be expected. These can be assumed to provide, as corrosion progresses, increasing resistance to diffusion of nutrients as well as other species and consequentially produce a gradually declining rate both of microbiologically influenced and abiotic corrosion. The result is the polarization of the corrosion rate, as seen in phase 3 (Fig. 1).

Phase 4 of the model is based on compendium of empirical observations [4], including those reported by Forgeson et al. [16] and by Southwell et al. [17] for exposures of steels up to 16 years in tropical seawaters. These data show that after about 1–1.5 years exposure, which corresponds in these cases to the end of phase 3, the corrosion loss as a function of time can be modelled as a linear function [4]. The relatively low value of the long-term rate of corrosion in phase 4 has been attributed to the effect of accumulated corrosion products reducing diffusion, counteracted to some degree by losses of outer rusts caused by slow erosion and by occasional shedding of rusts. Some empirical evidence exists for these mechanisms [18]. On the basis of these observations, it will be assumed for the present purposes that the model of Fig. 1 can be simplified to the linear functional relationship shown in Fig. 2 for long-term exposures. It consists primarily of the linear function B–C representing long-term progression of corrosion (phase 4 in Fig. 1) but extended back to A at  $t = 0$ . A model similar to A–B–C was first suggested by Southwell et al. [19]. It was based only on empirical corrosion loss data from the Panama Canal Zone. A refinement is to approximate also the rate of early corrosion loss, modelled as linear function 0–D. Herein only the linear function A–B–C is considered.

Unlike the conventional average ‘corrosion rate’ the linear function A–B–C does not pass through the origin. It may be parameterized by  $c_s$  and  $r_s$  that describe the intercept of the linear function on the corrosion loss axis and the slope of the linear function respectively. Both parameters  $c_s$  and  $r_s$  are functions of mean seawater temperature, at least for unpolluted and aerated coastal seawaters with low water velocity and wave action typical for such waters [4,14]. The neglect of phases 0–3 in the simplified model is appropriate for exposure durations in excess of about  $2 \cdot t_a$  (see Fig. 1) where  $t_a$  was defined earlier as a function of seawater temperature [4]. In tropical waters  $t_a$  typically is less than one year and it is about 3 years in temperate waters such as in the North Sea. In the following, data recently available in the literature are used to evaluate  $c_s$  and  $r_s$  as functions of both average seawater temperature and the DIN concentration in the bulk seawater adjacent to the steel.



**Fig. 2.** Schematic simplification of the model in Fig. 1 for long-term corrosion as a long-term linear function parameterised by  $c_s$  and  $r_s$ . This simplification is valid for  $t > B$ . Also shown is that the initial corrosion rate  $r_0$  is an approximation to Fig. 1 for only for a short time.

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