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Corrosion of Mild Steel in Elevated Temperature Hard Freshwater

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Abstract

The bi-modal model previously shown to be applicable to long-term corrosion loss of mild steel in seawater is examined herein for hard fresh water at elevated temperatures. Laboratory data reported in the literature [are re-interpreted using conventional corrosion theory and the bi-modal model](#). The data fit the trends for the parameters of the model extrapolated from water temperature observations. One different set of data earlier can be reconciled if allowance is made for that the effect on corrosion of water velocity. Overall the results show the bi-modal model is applicable to fresh waters to 70°C.

Keywords: A. Steel; B. weight loss, modelling studies; C. high temperature corrosion, microbial corrosion.

1. Introduction

Corrosion of mild steel at elevated water temperatures and in particular in hard fresh waters is of practical interest. Applications include ships operating in tropical freshwater lakes or in tropical brackish waters and storage and piping of fresh water, for example for drinking water supplies and heating and ventilation units. Perhaps surprisingly, there appears to be very little data in the open literature for the corrosion of fresh waters at elevated temperatures [1]. This was confirmed in discussions with industry experts who noted that while confidential data for longer-term comparative corrosion tests for hot water systems is held by individual companies, they tend to be unwilling to divulge their proprietary information.

Recently one set of data was reported by Chernov et al. [2] for corrosion losses of mild steel in hard fresh water exposed for up to 1.5 years in a steel storage tank in a solar heating plant in Vladivostok, Russia. The water temperature was in the range 50-60°C, there was very slow water circulation, and stratification of dissolved oxygen was observed. This data together with subsequently obtained data for exposures to 2 years was examined for consistency with the corrosion loss model proposed earlier for mild steel in seawater, brackish water and fresh water [3]. For convenience the model is reviewed below. The analysis showed reasonable agreement overall but that there were some inconsistencies in detail between two of the parameters derived from the data and those predicted by extrapolation of the parameters of the model [4]. In the following, that analysis is reconsidered,

using primarily a set of laboratory observations reported by Mercer and Lumbard [5] for the corrosion of mild steel in hard Teddington tap water at 70°C. The model parameters extracted from that data are shown to be consistent with the trends for the parameters describing the early (shorter-term exposures) part the bi-modal model. The Vladivostok data is then re-examined and it is proposed that this data may be reconciled with the model provided allowance is made for the known effect of low water velocity of shorter-term corrosion losses. This reconciliation allows the proposition that the available evidence supports the applicability of the bi-modal model to the corrosion loss of steel both in hard freshwaters and in seawaters heated up to 70°C.

2. Review of bi-modal model

The bi-modal corrosion model is shown in schematic form in Fig. 1. It was proposed originally for seawater immersion corrosion loss [6] and may be considered a refinement of the well-known power law model used extensively in the atmospheric corrosion literature and for describing early progression of pit depth with exposure time [7]. The model of Fig. 1 has been shown to be consistent with a wide range of published data both for corrosion loss and for pitting, including a variety of low alloy steels and chromium steels and for a range of exposure conditions including brackish and fresh waters [8].

Figure 1.

The model is composed of 5 sequential phases each describing a different dominant corrosion mechanism. These are summarised in Fig. 1(a). The principal corrosion rate-controlling mechanism in the period $0 < t < t_a$ is diffusion of oxygen through the increasing thickness (and hence reducing permeability) of the rust layers. The effect of the availability of oxygen, expressed through the bulk water dissolved oxygen concentration [O], is shown schematically in Fig 1(b). More details are available [8]. Also shown, schematically, in Fig 1(b) is the effect of water temperature, which is an important influencing factor for most model parameters [6,8]. The terms r_0 , t_a , and c_a parameterise the early part (the first ‘mode’) of the model, with r_0 denoting the nominal ‘initial’ corrosion rate in the short period immediately after $t = 0$, t_a is the time point at which there is an up-swing in the corrosion rate (and the commencement of the second ‘mode’), and c_a denotes the corresponding corrosion loss at that time. The parameters for the later part of the model are not of particular interest for the exposition to follow. To be sure, estimation of these parameters involves a degree of subjectivity but despite this a high degree of consistency of the parameters has been found across many sets of data [6,8].

The development of the model included the likelihood that microbiologically influenced corrosion (MIC) plays a role in the corrosion process. As summarized earlier [8] this is known to be a factor particularly in phases 0 and 3 and to a lesser extent in phase 4 of the model, at least for seawater corrosion [8]. The effect of MIC on freshwater corrosion is much less known but has been seen previously in laboratory studies over exposure periods up to 12 months [9]. Whereas in seawater the bacteria most commonly associated with MIC are the sulfate reducing bacteria (SRB) whose metabolism (and growth and activity) is governed by nutrient (and energy) availability and in particular nitrogen availability, for fresh water the limiting nutrient(s) usually are sulfates, unless there is significant sewage or similar nutrient pollution [10]. Calcium carbonate in hard waters is thought to reduce the

availability of sulfates [11], depressing the metabolism of bacteria and thus reducing short-term corrosion rates. This explains why moderate changes in nutrient levels can cause significant increases in corrosion, inconsistent with changes in the rate of (electro-)chemical corrosion to be expected from direct changes in the chemical composition of the water. The bacteria involved in freshwater corrosion also are different [12,13].

Separately from any effect water hardness may have on the availability of nutrients, the calcium and magnesium carbonates primarily responsible for water hardness tend to deposit within the corrosion product layer formed on metals exposed to waters with high concentrations of these carbonates [14]. This is the case for seawater (which usually is supersaturated with carbonates) and also for hard fresh waters. The carbonates contribute to the formation of adherent, protective calcareous deposits at cathodic areas, particularly at higher pH [14,15]. The deposits have a relatively high electrical resistance and hence reduce the effective cathodic area, thereby reducing corrosion currents and hence corrosion. Equivalently, the effect can be described as the carbonates tending to reduce the diffusivity of the rusts on the corroded surface thereby reducing the rate of supply of oxygen and hence reducing the corrosion rate. Evidently, this effect is a direct function of water pH, a matter recognized already many years ago. One result is that so-called 'soft' waters (those with low levels of dissolved carbonates) can be very corrosive, irrespective of chloride content [3].

The parameters for the early part of the model have previously been estimated for mild steel exposed in natural seawaters below 29°C, based on a large number of field observations [3]. Trends for these data have been derived and are used below for comparison to data at higher water temperatures.

3. Warm Water Corrosion Data

As noted, there is very little data in the open literature for the corrosion of fresh waters at elevated temperatures [1]. As part of a much wider laboratory study, Mercer and Lumbard [5] reported various corrosion loss data for mild steel immersed continuously in fully oxygen-saturated Teddington tapwater at various temperatures in the range 5-95°C. The water was hard, [had a low chloride content and pH \$\approx 8.3\$ \(Table 1\)](#). The specimens were 15 mm diameter circular mild steel coupons, 40 mm long, rotated at 1 Hz. Several tests were conducted with different water temperatures and dissolved oxygen contents but only one set of data (at 70°C) was reported in sufficient detail to construct a curve of mass loss as a function of exposure period (Fig. 2).

[Table 1.](#)

Figure 2.

In Fig. 2 the best fit smooth trend curve was constructed through the data using the Stineman function, a locally weighted (10% of data) least squares fit [16]. Evidently, the resulting corrosion-loss function trend is consistent with Fig. 1. From Fig. 2 estimates were made for the parameters t_a , r_0 and c_a at 70°C.

There is insufficient information in Mercer and Lumbard [5] to construct corrosion mass loss curves such as Fig. 2 for other water temperatures in the range 29-70°C. However, they do quote corrosion losses at 49 days exposure for a number of different water temperatures T in the range 0-95°C (Fig. 3) and remarked that the data appeared to show 'no clear systematic behaviour'. However, with the aid of Fig. 1 [and well-accepted corrosion theory principles](#) a rational explanation is possible. Consider the 'exposure window' shown in Fig. 1(b) at t_i with $dt \rightarrow 0$,

and also the variation in the corrosion loss curve as the water temperature T increases. The corrosion loss curve moves to the left and in doing so the principal model corrosion phase observed in the window changes from phase 1 to phase 2. From this it can be deduced that c_a is sensitive to T in phase 1 but rather insensitive to T in phase 2. Thus in Fig. 3 the mass losses for $T < 25^\circ\text{C}$ refer mainly to phase 1 and those in the range $25^\circ\text{C} < T < 80^\circ\text{C}$ mainly to phase 2. At higher water temperatures the solubility of oxygen in water reduces quickly and the corresponding mass loss observations cannot be compared with those for lower water temperatures [5]. The data shown in Fig. 3 can be converted readily from mass loss per unit area to corrosion loss in the range $30\text{-}70^\circ\text{C}$ and in turn interpreted as c_a .

Figure 3.

Mercer and Lumbard [5] also quote measurements of corrosion potentials E as a function of water temperature T (Fig. 4). They state that the potentials may be interpreted as proportional corrosion rates when corrosion is under cathodic control, as is implicit in the model of Fig. 1. This is consistent with Evans diagrams in accepted corrosion theory [7]. As a result, the (logarithm of the) corrosion rate i is proportional to E . This allows the data points for $30 < T \leq 70^\circ\text{C}$ to be calibrated to corrosion rates in mm/yr., shown at right on Fig. 4.

Figure 4.

Apart from one value of model parameter t_a at 70°C that can be estimated from Fig. 2, there is no information in Mercer and Lumbard [5] that can be used to provide estimates of t_a at other water temperatures.

4. Discussion

The trends for the model parameters for the early part of the model have been estimated previously for mild steel exposed in natural seawaters below 29°C , using a large number of field observations [6]. Fig. 5 shows the trend for the parameter c_a for seawater exposures and also the results and trends for mild steel exposed to hard fresh waters [3]. The two data sets and trends are very similar. As a function of average water temperature T the trend for c_a can be represented mathematically, for each data set, by a shifted exponential function:

$$c_a = A \exp(-BT) + C \quad (1)$$

where A , B and C are constants obtained by fitting Eqn. (1) to data. Fig. 5 shows the trends extrapolated from 29°C to 70°C . It also shows the estimated value for c_a derived from the Teddington corrosion loss curve given in Fig. 2 as well as the value of c_a earlier estimated for mild steel in hard fresh water in the range $50\text{-}60^\circ\text{C}$ in a solar heating plant in Vladivostok, Russia [4].

Figure 5.

The same data sources [3,6] for waters below 29°C were used to obtain the extrapolated trends for the initial corrosion rate r_0 for seawater corrosion and for freshwater corrosion, in each case for waters in the pH range 7.5-8.5 taken as one data set (Fig. 6). In this case an Arrhenius relationship is used to fit a trend curve to the data, as is appropriate for temperature effects. Although there is considerable scatter in the freshwater corrosion data below 29°C , the two extrapolated trend curves fall remarkably close together. Figure 6 also shows the estimate of r_0 from

Fig. 2, and the estimates for r_0 given in Fig. 4 for parameters derived for the water temperatures used in the Mercer and Lumbard [5] experiments. The estimated value of r_0 for the Vladivostok data [4] is shown also. It is considerably lower in value than the trends.

Figure 6.

Figs. 5 and 6 show that the parameters derived from the interpretation of the Teddington hard water corrosion experiments provide, for c_a and r_0 respectively, values that are consistent with the respective trend curves extrapolated from the data for below 29°C. It is clear that they are consistent with a smooth transition of these parameters from those in cooler waters to those at 70°C. This should be expected as there are no obvious sudden or non-smooth changes in the corrosion processes.

The trend for t_a extrapolated to 70°C, is shown in Fig. 7. The trend shown differs somewhat from that given earlier [4]. Previously a difference was found between the trends for seawater and for freshwater at about the same pH at water temperatures around 25-30°C. Closer examination of the data showed that this difference was due entirely to one value for t_a estimated from the corrosion loss curve for field exposure at 27.6°C at Coco Solo, in the Panama Canal Zone [17]. A reassessment of the interpretation of the data for this site and its consistency with other sites of similar water temperatures led to a lowering of the estimated value for t_a , sufficient for it to fall in line with the other data for similar seawater exposures and with data for freshwater exposures. As a result only one trend line is shown in Fig. 7.

Figure 7.

Fig. 7 also shows the value of t_a estimated from Fig. 2 for Teddington fresh water. As noted, there is no other information in Mercer and Lumbard [5] that can be interpreted as applicable to estimation of t_a . This is understandable as that parameter had not yet been proposed at the time the experiments were conducted. Nevertheless, from Fig. 1 it is observed that t_a is related to r_0 , with lower r_0 producing longer values of t_a . This indicates that the trend for t_a should be inversely proportional to that for r_0 . Given the gradual changes in r_0 shown in Fig. 6, a gradual change from the value of t_a below 30°C to the value shown at 70°C can be assumed and this is also predicted in the trend line shown. Thus, while there is only one direct data point for t_a (i.e. that at 70°C) for water temperatures above 29°C, the trend shown in Fig. 7 can be considered reasonable and consistent with the (limited) available data.

Overall, the correspondence between the parameter values derived from the Teddington experimental observations and the respective trends may be considered remarkable, given the very considerable extrapolation that is required from the data in the range 0-29°C. However, the values of t_a and r_0 estimated earlier from the Vladivostok data [4] clearly are at odds with the trends in Figs. 6 and 7. The likely reasons for this are discussed next.

The Vladivostok data [2] was obtained from mass loss measurements for mild steel (CT-3) immersed for up to 2 years in very low velocity, hard fresh water at 50°C. The previous analysis showed that the data did not fit the trends particularly well although the bi-modal behaviour was clearly evident [4]. It is noted that the Vladivostok data was obtained in-situ. In normal scientific experiments much effort is devoted to ensuring standardised, well-controlled and reproducible experimental conditions. This seldom can be achieved for in-situ observations. It could be one reason for the Vladivostok model parameters showing the noted departures from the expected

trends. However, careful consideration suggests that water velocity is the influence most likely to have caused the departures. There are two grounds for this observation. First, the corrosion field observations for waters below 29°C were all for natural freshwater streams and coastal seawaters and these waters all have non-negligible water velocities. Previously it was estimated that for coastal seawaters the average water velocity is in the range 0.05 - 0.15 m/s, although this may vary considerably, both daily and seasonally, and may be much higher for short periods [18]. Second, the Teddington results were obtained for specimens rotating at a constant angular velocity (see above). For the 15mm diameter specimens this corresponds to a constant tangential velocity of about 0.05 m/s which is comparable with the typical water velocities in natural exposures. In contrast, the Vladivostok observations were made in water for which the water velocity was very low to negligible. Water velocity is well-known to have an effect on the rate of corrosion [18], as was also demonstrated by Mercer and Lumbard [5] for short-term exposures.

Increased water velocity has been shown earlier to have most effect while there is little or no corrosion product on the surface of the steel [18]. High water velocity reduces the thickness of the oxygen concentration gradient immediately adjacent to the metal surface when it is first exposed [19]. Conversely, in quiescent waters, such as in the Vladivostok experiments, the thickness of the oxygen concentration gradient is reduced at a lower rate and as a result the rate of early corrosion will be lower, consistent with the lower initial corrosion rate r_0 shown for Vladivostok in Fig. 5.

Water velocity has much less effect on c_a . The generation of new rusts tends to occur predominantly within the already existing rust layer, which is known to build up within a short period of time after initial exposure [19]. Although not all corroded metal is converted to deposited rust [20], in time there will be sufficient rust build-up to reach the end of phase 2 (Fig. 1) and thus the corrosion loss c_a at time t_a . In phase 2 the corrosion rate is governed by the diffusion of oxygen through the rust layers [8]. It follows that provided the diffusion characteristics of these rusts are not significantly different between the various coupons and for different water velocities, the value of c_a will not be influenced significantly by water velocity. This assumption is consistent with earlier observations [18]. It is supported by the Vladivostok data showing the parameter c_a close to the trend line (Fig. 5).

Turning now to t_a deduced from the Vladivostok experiment (Fig. 6), it is noted that as the water velocity reduces and as r_0 also reduces, the progression from phase 1 to phase 2 and from phase 2 to phase 3 is delayed (Fig. 1). Thus the corresponding time point t_a at which the change occurs from phase 2 to phase 3 also will be delayed. This is consistent with the low value of the Vladivostok data point (Fig. 6) for t_a relative to the trend line. Overall, these observations show that the parameters derived from the Vladivostok data are generally consistent, provided allowance is made for the effect of the low water velocity on that data.

CONCLUSIONS

1. For the corrosion of mild steel in hard fresh water in water temperatures in the range 30-70°C and at moderate water velocities the few available data show consistency with the aerobic part of the bi-modal model previously proposed for marine immersion corrosion at much lower water temperatures.
2. Other, previously reported, data under very low water velocity conditions also show overall consistency with the bi-modal model and its parameters, provided allowance is made for the known effect of water velocity on model parameters.

3. The present analysis extends the range of applicability of the bi-modal model to higher water temperatures for fresh hard water and, by implication, also for seawater.

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Figure 1. (a) Schematic corrosion loss model showing phases controlling corrosion and the model parameters t_a , r_0 and c_a , (b) the effect of reduction in dissolved oxygen content and the effect of increasing water temperature. Also shown is the 'exposure window' discussed in the text.

Figure 2. Mass loss data and best fit trend (see text) for corrosion loss as a function of exposure period for rotating mild steel coupons exposed in 70°C hard fresh Teddington (UK) water. Data from [5].

Figure 3. Mass loss as a function of water temperature at 49 days exposure reported by Mercer and Lumbard [5] showing that lower water temperatures are associated with phase 1 of the corrosion loss model (Fig. 1) and waters in the range 30-70°C with phase 2. Results for higher water temperatures are influenced by reduced oxygen solubility. The right axis shows the interpreted equivalent corrosion losses that, for phase 2, can be interpreted as c_a values.

Figure 4. Corrosion potential E as a function of water temperature at 49 days exposure based on data reported by Mercer and Lumbard [5]. The trend curve is a best fit. The equivalent initial corrosion rates r_0 are shown on the right axis and calibrated, as shown, at 30 and 70°C.

Figure 5. Plot of trends for parameter c_a as a function of average water temperature T , derived from data in the range 0-29°C and extrapolated to 70°C. The values of c_a derived from the Teddington corrosion loss curve at 70°C, taken from Fig. 2, and the 6 estimates at 40, 60 and 70°C taken from Fig. 3, are shown. Also shown is the c_a estimate for the Vladivostok data.

Figure 6. Plot of trends for the initial corrosion rate r_0 as a function of average water temperature T , derived from data in the range 0-29°C and extrapolated to 70°C. The value of r_0 derived from the Teddington corrosion loss curve at 70°C, taken from Fig. 2, and the 6 estimates at 40, 60 and 70°C taken from Fig. 4, are shown. The r_0 estimate for the Vladivostok data is shown also.

Figure 7. Plot of trend for parameter t_a as a function of average water temperature T , derived from data in the range 0-29°C and extrapolated to 70°C. The value of t_a derived from the Teddington corrosion loss curve at 70°C (Fig. 2) is shown. The value of t_a estimated for the Vladivostok data is shown.

Table 1 Water Quality Data

	Teddington water	Vladivostok water
Reference	[5]	[2]
Temperature °C	30, 40, 60, 70 °C	50 – 60 °C
Dissolved Oxygen	‘fully saturated’	5.9 mg/L
Total alkalinity	2.76 mmol/L (276 ppm CaCO ₃)	0.5-0.6 mmol/L
Chlorine content	‘low’ (approx 40 ppm)	‘low’
pH	8.3 (approx)	8.7-9.2