High Temperature Hard Freshwater Corrosion Loss of Mild Steel

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Abstract

Some maritime structures may be exposed to higher temperature freshwaters and these can cause significant corrosion. Data obtained in a realistic experiment in which mild steel coupons were exposed for up to two years to hard freshwater at temperatures in the range 50-60°C are described and interpreted relative to the corrosion loss model earlier shown to be applicable to both seawater and fresh water corrosion. The model is reviewed briefly. It considers cathodic oxygen depolarization in the early stages of corrosion and the development of anoxic conditions that could permit the involvement of bacteria in the corrosion process. It is shown also that corrosion loss data for the hard tap water from Teddington, UK at 70°C is consistent with the corrosion loss model. The trends derived from these data permit improved estimates to be made of the effect of water temperature on the longer-term corrosion loss of mild steels in both hard fresh waters and seawaters.

Keyword: Corrosion, steel, water hardness, high temperatures, long-term.

1. INTRODUCTION

Although many marine structures are exposed to saline environments, this is not always the case, for example ships operating in freshwater lakes and coastal vessels operating mainly in brackish and river waters. Also, corrosion issues can arise with the storage and piping of fresh water, for example for drinking water supplies and heating and ventilation units. Earlier, Chernov et al. \cite{1} described corrosion loss data for 1.5 years of exposure of a steel storage tank for a solar heating plant in Vladivostok, Russia, for which the hard water circulating slowly through it was in the temperature 50-60°C and with stratified dissolved oxygen levels. Subsequently, data for exposures to 2 years at the same facility became available and these were analysed in terms of the corrosion loss model summarised in Figure 1 \cite{2}.

![Figure 1. Schematic corrosion loss model showing phases controlling corrosion, some of the model parameters, the effect of reduction in dissolved oxygen content and the effect of increasing water velocity.](image-url)

The model in Figure 1 was proposed originally for seawater immersion corrosion loss \cite{3}. It has since been shown to be applicable also for pitting and for a range of exposure conditions including brackish and fresh waters \cite{4}. The model is composed of 5 sequential phases each describing a different corrosion mechanism. These are summarised in Figure 1. Cathodic oxygen depolarization is the principal corrosion rate-controlling mechanism in the period $0 < t < t_a$. The effect of the availability of oxygen, expressed through the bulk water dissolved oxygen concentration $[O]$, is shown schematically. More details are available \cite{5}. Also shown, schematically, is the effect of water temperature \cite{3,4}. The terms $r_0$, $t_a$, and $c_a$ parameterise the early part of the model, with $r_0$ denoting the
nominal ‘initial’ corrosion rate in the period immediately after $t = 0$, $t_a$ is the time point at which there is an up-
swing in the corrosion rate, between phases 2 and 3, and $c_a$ denotes the corresponding corrosion loss at that time.
All parameters are functions of water temperature $T$ [3].

In the development of the model it was assumed that microbiologically influenced corrosion (MIC) plays a role in
the corrosion process and in particular in phases 0 and 3 and to a lesser extent in phase 4. The influence of
bacteria on seawater corrosion is well-known [5]. Its effect on freshwater corrosion is much less known but has
been seen previously in laboratory studies over exposure periods up to 12 months [6]. In seawater the bacteria
most commonly associated with MIC are the sulfate reducing bacteria (SRB). The metabolism (and growth and
activity) of bacteria tends to be governed by nutrient availability. In seawater nitrogen usually is the limiting
nutrient since the nutrients carbon, iron and sulfates are supplied respectively by other organic matter, the
corrosion process and the seawater content of sulfates. However, for fresh water the limiting nutrient(s) usually
are sulfates, unless there is significant sewage pollution. Calcium carbonate in hard waters is thought to reduce
the availability of sulfates [7], depressing the metabolism of bacteria and thus reducing short-term corrosion rates.
This also explains why moderate changes in nutrient levels can cause significant increases in corrosion,
inconsistent with changes in the rate of corrosion to be expected from direct changes in the chemical composition
of the water [8]. The bacteria involved in freshwater corrosion also are different [9,10].

Separately from any effect water hardness (due to calcium and magnesium carbonates) may have on the
availability of nutrients, calcium and magnesium carbonates tend to deposit within the corrosion product layer
formed on metals exposed to waters with high concentrations of these carbonates. 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 [11]. 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 [12].

In the following, the previous work will be reviewed and then compared with data for exposure of mild steel
coupons at 70°C in hard tap water sourced from Teddington, UK [13]. It will be shown that the model parameters
are very similar for sea and for hard water. This should be expected since, as noted, seawater is normally
supersaturated with carbonates. It is then shown that the data used in the earlier study together with the data for
Teddington permits a more consistent and internally coherent interpretation to be given for the effect of high
water temperatures on the corrosion loss of steel in hard freshwaters and also in seawaters.

REVIEW OF EXPERIMENTAL OUTCOMES

The corrosion loss derived from mass loss measurements for mild steel (CT-3) immersed for up to 2 years in hard
fresh water is shown in Figure 2. It shows three different curves, corresponding to three levels of dissolved
oxygen content, ranging from close to fully saturated (0.59 mg/l) down. These dissolved oxygen levels
correspond to different depths of immersion in the exposure tank. The water hardness was in the range 0.5-0.6
mmol/l (total alkalinity) and pH in the range 8.7-9.2. Tests showed some dissolved nutrients in the water. The
corrosion loss curve previously was found to be generally consistent in form with that of the model shown in
Figure 1 [2]. This does not prove that the data is consistent also with the phases noted for Figure 1, but it is
certainly plausible. Figure 2 shows 3 sets of results. There was a fourth, for an intermediate dissolved oxygen
concentration level that was not completely consistent, although it demonstrated the same corrosion loss trend as
a function of time [2]. The locus curve for $t_a$ shown in Figure 2 indicates consistency between the mass loss
curves. In the following, attention will be focussed on the upper curve in Figure 2, that with the highest) dissolved
oxygen concentration.

Figure 3 shows data for $t_a$ used previously to attempt to place the results for CT-3 at 50°C in context. That earlier
data consisted of values for $t_a$ derived from corrosion loss curves for a large number of field observations for
seawater (which is normally very hard owing to the near saturation of carbonates). Also shown are results derived
from corrosion loss curves for mild steel exposed to hard fresh waters. These latter data are seen to be essentially
indistinguishable from the seawater data.
Figure 2. Corrosion loss trends based on piece-wise best fitting to data points obtained from mass loss measurements data, for three different levels of dissolved oxygen. Data from [1].

Figure 3. Plot of trend for parameter $t_a$ as a function of average water temperature $T$, derived from data in the range 0-29ºC and extrapolated to 70ºC.

In Figure 3 both data sets are for water temperatures below 29ºC [4]. Since the data for seawater and for the freshwater are indistinguishable in Figure 3, it was considered appropriate to combine them for the purpose of fitting a mathematical expression to represent the trend. Previously [2,3] a simple exponential function appeared to provide an appropriate fit between corrosion loss $c(T)$ as a function of average water temperature $T$, but in the present case a shifted exponential function was found to be more appropriate. It has the form

$$c(t) = A \exp (-B T) + C$$

(1)

where $A$, $B$ and $C$ are constants obtained by fitting (1) to data.

The trend shown in Figure 3 was obtained by fitting this function to the corrosion loss data for waters of average temperatures 29ºC and less. The function was then extrapolated to 70ºC. Figure 3 also shows, at 50ºC, the value of $t_a$ estimated from Figure 2 for the highest dissolved oxygen Vladivostok fresh water exposure data. Clearly this value for $t_a$ is considerably greater than expected from the trend extrapolated from the data.

The plot for $t_a$ in Figure 3 differs somewhat from that given earlier [2]. The reason for this is that previously a difference appeared to exist between the trends for seawater and for freshwater at about the same pH, particularly at water temperatures around 25-30ºC. Closer examination of the data showed that this difference was due almost entirely to one value for $t_a$ estimated from the corrosion loss curve for field exposure at 27.6ºC at Coco Solo, in the Panama Canal Zone [14]. 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. As a result only one trend line is now sufficient.

In the earlier work [2] trends were obtained also for the initial corrosion rate \( r_0 \) and for the corrosion loss \( c_a \) at around \( t_a \) (see Figure 1). Figure 4 shows the earlier data for \( r_0 \) for seawater corrosion and for freshwater corrosion for waters in the pH range 7.5-8.5 taken as one data set, all for water temperatures below 29ºC. Evidently there is considerable scatter in the freshwater corrosion data. Also shown are the trends drawn through the data sets and extrapolated to 70ºC. Despite the scatter in the freshwater data the trends for \( r_0 \) are remarkably close together. However, the value of \( r_0 \) estimated for the highest dissolved oxygen content corrosion loss trend for Vladivostok data (Figure 2) is much below the extrapolated trend. This was noted earlier [2] but no explanation was offered. An explanation will be offered below.

![Initial Corrosion Rate](image)

**Figure 4.** Plot of trend for the initial corrosion rate \( r_0 \) as a function of average water temperature \( T \), derived from data in the range 0-29ºC and extrapolated to 70ºC.

The third parameter, \( c_a \), is shown on Figure 5, again with the data for average water temperatures below 29ºC used to construct shifted exponential curves both through the seawater data and the freshwater data in the pH range 7.5 - 8.5. The curves have been extrapolated to 70ºC. They are remarkably consistent. The data point for the Vladivostok experiment is shown also and is consistent with the extrapolated trend.

![Parameter \( c_a \)](image)

**Figure 5.** Plot of trend for parameter \( c_a \) as a function of average water temperature \( T \), derived from data in the range 0-29ºC and extrapolated to 70ºC.
ADDITIONAL OBSERVATIONS

Using data obtained only in the range 0-29°C to estimate trends at 50°C and 70°C represents a very considerable extrapolation that might be expected to have a significant degree of uncertainty. This may be a reason for the Vladivostok data not fitting the trend curves for $t_a$ and $r_0$ as well as might have been expected. To attempt to throw some light on this, recourse was made to a set of shorter-term data for mild steel immersed continuously in fully oxygen-saturated Teddington tapwater at 70°C [13]. The water was hard (total hardness 276 ppm as CaCO$_3$), had a low chloride content (Cl$^-$ 40 ppm) and a $p$H $\approx$ 8.3. The exposure experiments were carried out in small test vessels causing the pH of the water to increase somewhat during the tests. The corrosion specimens were 15 mm diameter circular mild steel coupons, 40 mm long, rotated at 1 Hz and exposed for up to 101 days. Several tests were conducted with different water temperatures and dissolved oxygen contents but only one set of data was reported in sufficient detail to construct the mass losses shown in Figure 6 as a function of exposure time. The best fit trend curve was constructed through the data using a weighted (±10%) Stineman function. It is evident that the resulting trend is consistent with Figure 1. From it estimates were made for $t_a$, $r_0$ and $c_a$ and these are plotted on Figures 3-5 respectively.

![Figure 6. Mass loss data and best fit trend for corrosion loss as a function of exposure period for rotating mild steel coupons exposed in 70ºC hard fresh Teddington (UK) water. Data from [13].](image)

For the Teddington data there are good fits for the parameters $t_a$ and for $c_a$ but less so for $r_0$. In the latter case, however, the estimated $r_0$ value is clearly in the expected region. Together these results should be considered remarkable, given the very considerable extrapolation from the data in the range 0-29°C to the much higher 70°C temperature relevant for the Teddington data.

DISCUSSION

In normal scientific experiments much effort is devoted to ensuring standardised, well-controlled and reproducible experimental conditions. This can seldom be achieved for in-situ observations. It could be one reason for the Vladivostok results showing some departure from the trends given in Figures 3 and 4. However, careful consideration of all the possible influencing factors suggests that water velocity is the influence most likely to have caused the difference between the Vladivostok observations and the trend obtained from the observations made elsewhere. The corrosion field observations for waters below 29°C were all for natural freshwater streams and coastal seawaters. These data all were obtained in waters that have non-negligible water velocities. In contrast, the Vladivostok observations were made in water for which the water velocity was extremely low (negligible).

Previously it was estimated that for coastal seawater the parameters for the model shown in Figure 1 correspond to an average water velocity in the range 0.1 - 0.15 m/s, although for most natural waters this typically varies considerably, both daily and seasonally, from negligible to much higher for short periods [15]. The Teddington results were obtained at constant velocities. When rotating at 1 Hz, the 15mm diameter specimens have a tangential velocity of about 0.05 m/s. This is comparable with the natural exposures.

Increased water velocity has been shown earlier to have most effect while the corrosion products are still insufficient to influence the rate of corrosion. Thus immediately upon exposure the effect of high water velocity is to reduce the oxygen concentration gradient immediately adjacent to the metal surface. This permits a higher rate
of oxygen diffusion out of the adjacent water (other factors equal) and, under cathodic control, this causes a higher corrosion rate. This will continue until such time when the build-up of corrosion products and the diffusion of oxygen through the layers begins to control the rate of corrosion. Conversely, when the oxygen concentration gradient is not depressed, such as would have been the case for the quiescent waters in the Vladivostok experiments, the rate of oxygen diffusion will be lower, with concomitant lower corrosion rate, both initially and later. This phenomenon is reflected directly in the lower than expected initial corrosion rate $r_0$ shown for Vladivostok in Figure 4.

Water velocity also is likely to have some influence on the rate at which the rusts build-up on the metal surface. However, the effect is unlikely to be great since the generation of new rusts tends to occur predominantly within the already existing rust layer. After a short period of time this is protected by the older external rust layers. The rate of oxygen diffusion to the corroding metal surface will reduce as the rust layer increases in thickness (even though it is known that some metal is not converted to deposited rust) and in time there will be sufficient rust build-up to reach the corrosion loss parameterised by $c_a$ in Figure 1. Evidently, this will not be significantly influenced by water velocity, for the reasons just considered. The consistency of the Vladivostok data with the trends shown in Figure 5 supports this argument.

Because $r_0$ is much lower for cases such as the Vladivostok experiment with negligible water velocity, the progression from phase 1 to phase 2 of the model (Figure 1) will be delayed in time. Moreover, the duration of phase 2 will be shorter in time than for higher water velocities because only a small change is required in diffusivity of the rust layers to reach the end of phase 2. The corresponding total time $t_a$ is the net result of an extended phase 1 and a shorter phase 2 (relative to normal conditions with non-negligible water velocity). The location of $t_a$ for the Vladivostok data shown in Figure 3 is consistent with this interpretation.

As noted in the earlier paper [2] one of the remarkably features revealed by the comparison between the corrosion losses for seawater immersion and for freshwater is that the parameters $t_a$ and $c_a$ for the earlier parts of the corrosion loss curves are essentially independent of salinity. Both parameters represent aspects of the longer-term progression of corrosion with time. Only $r_0$, representing the corrosion rate immediately upon first exposure and soon thereafter, shows a clear dependence on salinity (Figure 4). However, in most practical cases for which the water velocity typically is non-negligible, $r_0$ is of little overall importance since phase 1 of the model is relatively short. This also can be seen in data and trends for the effect of water velocity reported earlier [15]. The overall outcome is that for other than very short-term exposures salinity per se is not a significant influence on long-term corrosion loss. As already found earlier [4], water hardness is a key factor, both in short-term and in longer term corrosion. For the results discussed herein, however, water hardness and pH were similar.

CONCLUSIONS

The following conclusions may be drawn from the present study:

1. Data obtained over two years of exposure in hard fresh water at around 50°C and also over about 0.3 years at 70°C are consistent with the model previously proposed for marine immersion corrosion at much lower water temperatures.

2. It was found that hard fresh water and (hard) seawater exhibit very similar behaviour as a function of average water temperature, as measured by the parameters of the model.

3. Salinity per se, has little influence on long-term corrosion loss behaviour.

4. Account must be taken of water velocity conditions in comparing the model parameters as estimated from corrosion loss functions.

5. The data, trends and interpretations given herein extend the range of applicability of the model to much higher water temperatures, at least for fresh hard water and, by implication, also for seawater.

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REFERENCES