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Corrosion Loss of Mild Steel in High Temperature Hard Freshwater

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Abstract: This paper presents an interpretation of corrosion loss data for mild steel coupons exposed for up to 2.6 years to freshwater under a range of dissolved oxygen levels and temperatures 50-60°C. The water total alkalinity was 0.5-0.6 mmol/L and pH 8.7-9.2. It is shown herein that the data is consistent with [the early stages](#) of the corrosion loss model proposed earlier for steel exposed to seawater, brackish water or freshwaters in the usual environmental range of 0-30°C. The new data was found to be consistent with the effect of dissolved oxygen and the effect of water hardness on the model.

Keywords: A: Mild steel, B: Weightloss, C: High temperature corrosion, Microbiological corrosion.

Introduction

It is well-known that the rate of corrosion of steel exposed to waters with dissolved oxygen decreases owing to the build-up of corrosion products. This inhibits the rate at which oxygen can participate in the cathodic reaction and hence reduces its rate, a phenomenon known as cathodic or oxygen depolarization. The reduction in corrosion rate has been observed for field data and has been considered in a number of corrosion loss models [1]. Most of these are empirical or semi-empirical, requiring some degree of calibration. One of these, described earlier by Chernov and Pomorarenko [2], was used recently by Chernov et al. [3] to interpret corrosion loss data obtained over a period of 1.5 years in the tank-accumulators of a solar heating unit in [Vladivostok, Russia](#). They found that the corrosion loss [decreased with](#) depth in the tank, which in turn was related to dissolved oxygen (DO) concentration. [The water temperature, pH, water hardness and salinity were not considered in this analysis.](#)

A more complex corrosion loss model for steels has been described by Melchers [4]. It was initially proposed for seawater immersion corrosion but has since been shown to be applicable also to brackish and fresh waters [5] and for both ‘uniform’ and pitting corrosion [1]. It includes oxygen depolarization for the early stages of corrosion during which time also microbiological activity in the biofilm on the metal surface may contribute to corrosion [6, 7]. Unlike other models, the model in [4] allows for the possibility that eventually anoxic or suboxic conditions can develop at or near the corrosion interface and that these permit the possibility of bacterial activity [8]. This changes the corrosion process from oxygen depolarization to one influenced also by the effects of bacterial activity. It is usually marked by a distinct change in the development of corrosion loss with time, shown as occurring at t_a . Figure 1 shows a schematic version of the model together with a summary of the various (sequential) phases involved. These are labelled 0-4 and a summary description of the essential processes involved in each phase is shown. More details of these are available in [4,8].

Figure 1.

The effect of water temperature is important for the rate of oxygen depolarization and hence for the rate of corrosion loss. This follows from fundamental theoretical considerations [9] and has been demonstrated both in laboratory studies [10] and in field studies [4]. In particular, in carefully conducted studies lasting 72 days Mercer and Lumbard [10] observed that the early corrosion rate increased with increasing water temperature, up to about 70-80°C and then declined, the latter result attributed to the significant reduction in solubility of oxygen at high water temperatures. The early corrosion loss was shown to be consistent with Arrhenius behaviour, although this is not necessarily identical for different types of waters [11]. The influence of water temperature has been shown to be important also for the interpretation of corrosion losses for steels exposed to actual seawater immersion conditions and also to steels in brackish and freshwater immersion [5], at least for water temperature ranges normally encountered in natural environmental exposures (say to 30°C).

The importance of oxygen in the rate of corrosion has long been recognized from short-term experiments [9], including those by Mercer and Lumbard [10] who reported the direct, non-

linear but consistent dependence of mass loss on DO. The effect also has been considered for field immersion seawater corrosion observations and related model studies [12].

In the model of Figure 1 oxygen depolarization is the **principal** corrosion rate-controlling mechanism in the period $0 < t < t_a$. Figure 1 shows, schematically, the effect of the availability of oxygen at the corroding surface, for which a convenient surrogate is the bulk water dissolved oxygen (DO). Evidently, as the available oxygen at the corroding surface decreases, the early rate of corrosion (in phase1) will decrease and it also will decrease corrosion in phase 2, although not in a linear manner since oxygen diffusion in this phase is controlled also by the increasing thickness and hence reduced permeability of the rust layers as they build-up with continued corrosion [4].

The effect of the concentration in the **bulk** water of critical nutrients for bacterial metabolism and growth is shown in Figure 1, again schematically, consistent with recent work [7,13]. Finally, the model and each of the parameters t_a , c_a and r_0 that describe in particular the early part of the model are functions of water temperature [4]. Here r_0 denotes 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 is the corresponding corrosion loss at that time.

The immersion corrosion of steels is known to be influenced **also** by the pH and alkalinity of the water. Seawater is strongly buffered against pH changes owing to its high alkalinity from being (super-)saturated with CaCO_3 . Seawater corrosion products invariably show a high CaCO_3 content [14] and this tends to reduce the ability of oxygen to **diffuse** to the corrosion interface (i.e. it increases depolarization). The alkalinity of fresh (and brackish) waters depends on the water source and in particular the availability and rate of dissolution of CaCO_3 and MgCO_3 from rocks and soils in the various reaches of rivers from which water supplies are drawn. One result is that so-called 'soft' waters (those with low dissolved carbonates) can be very corrosive, irrespective of chloride content [5, 15].

In the following the mass loss and DO data given by Chernov et al. [3] for up to 1.5 years exposure are reviewed, together with additional mass loss data for up to 2.6 years exposure and by new data for mean water temperature and for water alkalinity. The data are then considered in terms of the model of Figure 1.

Experimental results

The corrosion tests were carried out in 2.0 x 0.9 x 2.2m deep tanks filled with fresh water flowing at negligible water velocity. The steel coupons 135 x 20 mm and 3 mm thick, with support holes centred 10mm from the top edge, were machined from St-3 grade steel which complies with Russian Standard GOST 380-94: Common quality carbon steel. Prior to immersion the coupons were code-marked for identification, cleaned using an inhibited 15% sulphuric acid solution followed by washing in distilled water and drying at 110°C and weighing to 0.00001g accuracy on analytical scales (Shimadzu AW220).

The coupons were immersed with their support holes at 25 ± 5 mm, 257 ± 12 mm, 930 ± 10 mm and 1485 ± 15 mm depths, with these ranges being the result slight variations in water level and the practicalities of installation of coupon supports. Usually one coupon was recovered for each depth at each time point (but sometimes two coupons were recovered - see Table 1). After recovery the coupons were immediately cleaned and weighed using the same procedure as before immersion. Mass loss was obtained by subtracting the initial mass from the final mass and corrosion loss calculated using the nominal density for steel and the volume of the coupons. The resulting error was estimated to be less than 0.1%. After cleaning, the coupons showed a predominance of uniform corrosion (Figure 2), with some localized evidence of anodic areas. Pitting was not observed for any of the coupons except sometimes around the fasteners. This was estimated as occurring over no more than 3-5% of the total surface area. The corrosion losses and other data are given in Table 1.

Table 1

Figure 2

The DO levels were measured at close to coupon mid-height using a portable electrochemical probe NI 9142 (Portugal). The water temperature was controlled by the solar collection system and was in the range 50-60°C throughout the test period. It was measured using a specially calibrated thermocouple.

Figure 3 shows the relationship between depth of immersion to the centre of the coupon and measured DO levels. A smooth continuous relationship should be expected, most likely of exponential form since DO is in dynamic equilibrium with oxygen in the air and involves diffusion through the waters above the depth considered. The DO at the surface (about 6 mg/l) is consistent with what would be expected. Comparing this with the trend through the other data suggests that the DO level at 930 mm depth is in error, and most likely should have been 2.3 or 2.4 mg/l rather than the 3.2 mg/l reported. The analysis presented below does not depend critically on this interpretation but does make it more consistent, as will become evident.

Figure 3.

The corrosion losses summarized in Table 1 are shown in Figure 4 as a function of exposure period and of the DO levels. Large symbols have been used for the data points to emphasize there is a (small) degree of uncertainty about them, mainly for corrosion loss. The centre of each symbol may be considered as the 'best estimate' based on the data in Table 1. The thin continuous lines are lines of best fit obtained with the curve-fitting routine provided with the computer-graphing program. Thus they may be considered to be 'objective' fits to the data. For the higher DO levels there is some inconsistency in the data between 0.915 years and 1.038 years of exposure since corrosion loss cannot decrease with time. The reason for this inconsistency in the data as reported is not obvious but could be due to bacterial influences, known from previous observations to cause a certain amount of randomness in coupon mass loss observations [16]. Nevertheless, the overall trends for mass loss are quite clear and consistent.

Figure 4.

Interpretation

The data points shown in Figure 4 can be interpreted in terms of the model of Figure 1. The resulting 'subjective' trends are shown with bold lines in Figure 4. On the whole they are very close to the thin lines produced by the computer routine, indicating that they are appropriate fits to the data. Nevertheless, at a detail level, some interpretation was required in fitting the bold curves through the data. In each case this could be achieved with an outcome that is

consistent with trends noted earlier for freshwater corrosion [5]. The slight inconsistencies in some of the data around one year exposure are relatively small and simply could be the result of natural variability in corrosion mass loss observations [16]. Collectively, the trends are consistent also with expectations for the effect of DO [12], with both corrosion loss at the transition time t_a and time to t_a reducing with lower DO. This trend is indicated schematically by the grey curve, which is the locus of the transition time t_a as a function of DO. Except for the curve for $[O] = 2.4$ mg/l, the value estimated from Figure 3, the grey line is a reasonable fit to the data at t_a . Overall, the locus indicates consistency in the effect of DO, as also seen in earlier experimental observations [12].

Ignoring the very short Phase 0, Figure 1 shows that the corrosion loss curve as a function of exposure period is approximately linear function only for relatively short exposure periods, corresponding essentially with phase 1 of the model [17], with the reduction of the corrosion rate occurring after a short time as a result of cathodic polarization, i.e. mainly during phase 2. The effect of DO on corrosion rate therefore can be seen directly only for short exposure periods, say to < 0.5 year in the present tests, when the rust layers play little or no role in determining the rate of corrosion. This can be seen in Figure 5. It shows corrosion loss plotted as a function of DO for two exposure periods (0.167 and 0.4 years). The trend lines are direct linear best fits obtained from the plotting program. They show that despite some minor variability in corrosion loss, for the short exposure periods considered here corrosion loss is closely a linear function of DO, as expected from first principles.

Figure 5.

It remains to consider the interpretation of the trend lines shown in Figure 4 relative to previous calibrations for the model parameters r_0 , t_a and c_a (Figure 1). These are available only for fully aerated waters with water temperatures less than 30°C [4]. This means that only the case with highest DO level (DO = 5.9 mg/l in Figure 4) can be considered. Previous work has shown that these parameters are, in the case of brackish and fresh waters, dependent on the bulk water pH, reflecting its alkalinity. Although not reported in Chernov et al. [3], the water pH and total alkalinity were measured at various times in the range pH 8.7-9.3 and 0.5-0.6 mmol/L respectively.

Figure 6 shows the trends for the parameter t_a as a function of mean water temperature and mean pH extracted earlier [5] from various field data. The curve for fresh water at pH = 8 has been extrapolated through the earlier data to $T = 50^\circ\text{C}$ using the observed (best estimate) value for t_a at $T = 50^\circ\text{C}$, together with the estimated error bar. It is seen that this value is generally consistent with the previous data for pH=8. Figure 6 shows that for water temperatures greater than about 30°C , t_a is almost insensitive to water temperature. There was insufficient data to construct relationship for higher pH values.

Figure 6.

The amount of corrosion loss that is expected when cathodic oxygen polarization has been significantly reduced is that at the end of phase 2 in the model of Figure 1. It is given by the parameter c_a . Earlier data for this parameter as a function of mean water temperature and pH are shown in Figure 7 [5], with the curve for fresh water at pH = 8 again extrapolated to $T = 50^\circ\text{C}$. The value of c_a for the upper curve in Figure 4 is about 0.4-0.5 mm. When this plotted on Figure 7 at $T = 50^\circ\text{C}$, together with the estimated error bar, it is seen that this is consistent with the trend for the parameter c_a at pH = 8.

Figure 7.

In the model of Figure 1, the parameter r_0 describes the initial corrosion rate. It is a function of mean water temperature (and hence of oxygen solubility in water) and of pH. It is also known to be a function of microbiological activity that commences, for seawater and also for somewhat polluted fresh waters almost immediately after first immersion [7]. The microbiological activity contributes to corrosion loss and this has been related to the availability of critical nutrients, including nitrogen and sulphates [8]. Previous analysis of the influence of pH and water temperature on the initial corrosion rate r_0 was based on few data and showed a considerable degree of uncertainty [5]. If all the data for higher pH is used, the relationships shown in Figure 8 is obtained. The value of r_0 for the Vladivostok data with highest DO can be estimated from the trend in Figure 4 at around $t = 0$. This indicates r_0 is about 0.065 mm/y. The modified trend with this value included (and with an estimated error bar) is shown also. It is evident that this trend is positioned significantly lower at higher water temperatures. As noted, this trend is likely to be the result at least in part of the reduced

solubility of oxygen in higher temperature seawaters.

Figure 8.

Discussion

Although considerable corrosion damage was observed already soon after taking the solar heating tank units into service [3], it is seen from the above comparisons to data obtained from a wide variety of other sources, extrapolated to allow for the higher water temperature and also considering the hardness of the water involved, that the observations are generally consistent with other relevant field observations. This is despite the lack of earlier corrosion loss observations at water temperatures above about 30°C.

As noted, there is some inconsistency in the DO levels applicable to one set of data. As can be seen from Figure 4, however, the curve for corrected DO concentration of 2.4 mg/l appears to be in the correct location relative to the other trend curves, but even if displaced upward slightly to place it where it would be for the DO concentration (3.2 mg/l) as originally reported, it is still roughly consistent with the other trend curves. Hence the apparent inconsistency of the DO level for this curve does not invalidate the arguments and comparisons made herein.

Apart from those marked 'seawater', the trend curves in Figures 6-8 are all for slightly brackish and fresh waters. Seawater is a very complex electrolyte for corrosion [14] and may provide corrosion mass loss results and hence corrosion loss trends different from those obtained for artificial seawaters. It follows that care must be taken in interpreting (and extrapolating) the trend for seawater in relation to the other trends shown in Figures 6 and 7 for brackish and fresh waters. Nevertheless, as seen in Figures 6 and 7, the trend curves for seawater are broadly consistent with the other trends. Figure 8 is the least satisfactory in terms of consistency with earlier data but careful examination of the earlier reported trends shows that there was very little information at higher water temperatures and that the water quality conditions for some of these were estimated. Taken together this suggests that the previous trends are unlikely to be sufficiently definitive to allow extrapolation with any degree of confidence. This can be seen both in the scatter of the data in Figure 8 and in the poor

trending capacity for that data. Evidently, considerably more experimental work is required to refine the trends for r_0 . Fortunately, in many practical situations the definition of r_0 is of interest mainly for short-term corrosion estimation. It has little influence on corrosion rate estimation in the longer term. In addition, knowledge of c_a and t_a and the general shape of the corrosion loss curve phases 1 and 2 of the model (Figure 1) will permit a rough estimate to be made of r_0 .

The data presented by Chernov et al. [3] does not extend sufficiently far in time to allow estimates to be made of the parameters that describe long-term corrosion [4]. At the present time there is insufficient information and data for these parameters to be estimated, for other than moderate seawater temperatures. During these experiment the possibility of there being a microbiological component to the corrosion of the steel coupons in the fresh water was not considered and measurements were not made of nutrient content. [However, it is known that Vladivostok drinking water has a significant bacterial and nutrient content \[18\].](#)

Evidently, there is considerable scope for experimental investigations to extend the present data base, and hence the modelling of corrosion loss, to situations with long-term exposures of steel. Such tests should examine a range of water temperatures, water hardness conditions and a variety of water bacterial and nutrient contents. [These should also consider the formation and types of rusts as this aspect has been shown to be relevant to the early stages of the model of Figure 1 and hence its parameters \[19\].](#)

Conclusion

The following conclusions may be drawn from the analysis presented herein.

1. Apart from a minor deviation from the expected variation of dissolved oxygen with depth for waters of low velocity the data supports the expectation that dissolved oxygen decreases systematically with water depth and directly influences the amount of corrosion loss observed at least while oxygen diffusion is the rate-limiting step in the corrosion process,
2. The interpretation of the mass loss data given herein shows that there is a defined period of time (0- t_a) during which the corrosion loss is governed by a (decreasing) rate of oxygen diffusion and that this defined period decreases with lower levels of dissolved oxygen

concentration. This is consistent with the proposed model.

3. The time to deviation from oxygen diffusion conditions for all dissolved oxygen levels was found to be consistent with trends established earlier for hard waters of much lower water temperatures. Similar consistency was found also for the corrosion loss at the end of the oxygen depolarization phase. However for the initial corrosion rate consistency with earlier work was found only in a very general sense.

4. The model for corrosion loss as a function of time, previously proposed based on data in the range 4-27°C, appears to be applicable for (hard) waters up to 50-60°C whilst the corrosion process is governed by cathodic depolarization. Calibration of the model and its extension to longer exposure periods at high water temperatures and for high water hardness awaits further investigation.

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References

- [1] R.E. Melchers, Development of new applied models for steel corrosion in marine applications including shipping, Proceedings, Conf. on Practical Design of Ships and Offshore Structures (PRADS), Houston, American Bureau of Shipping, Houston, USA, 2007: 919-927.
- [2] B.B. Chernov and S.A. Ponomarenko, Physiochemical modelling of metal corrosion in seawater, Protection of Metals 27(5) (1991): 612-615.
- [3] B.B. Chernov, O.P. Kovalev and A.V. Volkov, Corrosion prognosis for metals with oxygen depolarization, Protection of Metals, 44(3) (2008): 289-291.
- [4] R.E. Melchers, Modeling of marine immersion corrosion for mild and low alloy steels - Part 1: Phenomenological model, Corrosion (NACE) 59(4) (2003): 319-334.
- [5] R.E. Melchers, Modelling immersion corrosion of structural steels in natural fresh and brackish waters, Corrosion Science 48(12) (2006): 4174-4201.
- [6] B.J. Little, J.S. Lee and R.I. Ray, The influence of marine biofilms on corrosion: A concise review, Electrochimica Acta 54 (2008): 2-7.

- [7] E. Malard, D. Kervadec, O. Gil, Y. Lefevre and S. Malard, Interactions between steels and sulphide-producing bacteria - Corrosion of carbon steels and low-alloy steels in natural seawater, *Electrochimica Acta* 54 (2008): 8-13.
- [8] R.E. Melchers and R. Jeffrey, The critical involvement of anaerobic bacterial activity in modelling the corrosion behaviour of mild steel in marine environments, *Electrochimica Acta* 54 (2008): 80-85.
- [9] U.R. Evans, The corrosion and oxidation of metals: Scientific principles and practical applications, Edward Arnold (Publishers) Ltd. London, 1960.
- [10] A.D. Mercer and E.A. Lombard, Corrosion of mild steel in water, *British Corrosion Journal*, 30(1) (1995): 43-55.
- [11] R.E. Melchers, Ensuring validity and quality of deterioration models for structural reliability assessment, Proceedings, International Conference on Computational and Experimental Engineering and Sciences, (ICCES) Phuket, 9-13 April 2009, CDROM.
- [12] R.E. Melchers and R. Jeffrey, Early corrosion of mild steel in seawater, *Corrosion Science* 47(7) (2005): 1678-1693.
- [13] R.E. Melchers, The influence of seawater nutrient content on the early immersion corrosion of mild steel – 1 Empirical observations, *Corrosion (NACE)* (2007): 63(1) 318-329.
- [14] F.L. LaQue, Marine Corrosion, Wiley, New York, 1975.
- [15] H.H. Uhlig and R.W. Revie, Corrosion and Corrosion Control, 3rd Ed, John Wiley and Sons, New York, 1985: 12-15.
- [16] R.E. Melchers, Modeling of marine immersion corrosion for mild and low alloy steels - Part 2: Uncertainty estimation, *Corrosion (NACE)* 59(4) (2003): 335-344.
- [17] R.E. Melchers, Mathematical modelling of the diffusion controlled phase in marine immersion corrosion of mild steel, *Corrosion Science* 45(5) (2003): 923-940.
- [18] E.P. Ivanova, N.V. Zhukova, N.M. Gorshkova and E.L. Chaikina, Characterization of *Aeromonas* and *Vibrio* species isolated from a drinking water Reservoir, *J Applied Microbiology* 90 (2001): 919-927.
- [19] K.E. Garcia, A.L. Morales, C.A. Barrero and J.M. Grenache, New contributions to the understanding of rust layer formation in steels exposed to a total immersion test, *Corrosion Science* 48 (2006): 2813-1830.

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FIGURE Captions and Figures

Figure 1. Corrosion loss as a function of exposure time showing the various sequential phases (labelled 0-4) that develop with increased exposure time. Also shown are the effect of dissolved oxygen concentration for phases 0-2 and the influence of nutrient availability for the microbiologically influenced phases 3 and 4. There is also a small effect of nutrients on phases 0-1.

Figure 2. Typical samples of steel bars after cleaning showing the predominance of ‘uniform’ corrosion. There is evidence of local anodic areas particularly on coupon at right.

Figure 3. Relationship between water depth and oxygen concentration showing some inconsistency of the best fit data trend (broken line). The continuous trend is the expected trend for consistent data. R is the correlation coefficient.

Figure 4. Corrosion loss (estimated from mass loss) as a function of exposure period for 4 different dissolved oxygen (DO) concentrations, denoted $[O]$. The DO concentration shown as (2.4) is that estimated from Figure 3. The light curves were obtained as best fits from the plotting routine. The bold curves shown are trends interpreted from the data using Figure 1 as a guide. Large data points are used to emphasize a degree of uncertainty in corrosion loss (see text).

Figure 5. Corrosion loss as a function of DO for the shorter exposure periods. Lines are best fit trends.

Figure 6. The trend for the parameter t_a estimated from Figure 4 for $[O] = 5.9$ mg/l at 50°C in relation to the data trend obtained from various other field data [5]. The estimated error in t_a is shown by the error bar.

Figure 7. The trend for the parameter c_a estimated from Figure 4 for $[O] = 5.9$ mg/l at 50°C in relation to the data trend obtained from various other field data [5]. The estimated error in c_a is shown by the error bar.

Figure 8. The trend for the parameter r_o estimated from Figure 4 for $[O] = 5.9$ mg/l at 50°C in relation to the data trend obtained from various other field data [5]. The estimated error in r_o is shown by the error bar.

Fig 1

Fig 2

Note – this is the best available photograph.

Fig 3

Fig 4

Fig 5

Fig 6

Fig 7

Fig 8