NOVA

University of Newcastle Research Online

nova.newcastle.edu.au

Melchers, Robert E. "Long-term corrosion of cast irons and steel in marine and atmospheric environments" Corrosion Science Vol. 68, p. 186-194 (2013)

Available from: <http://dx.doi.org/10.1016/j.corsci.2012.11.014>

Accessed from: <http://hdl.handle.net/1959.13/1055032>

Long-term corrosion of cast irons and steel in marine and atmospheric environments

Robert E Melchers*

Centre for Infrastructure Performance and Reliability, The University of Newcastle, NSW 2308, Australia

Corresponding Author: * rob.melchers@newcastle.edu.au

Abstract

Long-term corrosion trends are important for assessing the remaining life of critical infrastructure. Herein the available literature data for grey cast iron and cast steel exposed to marine and to some atmospheric environments are shown to be consistent with the bi-modal model previously developed for steels. However, the development of the second mode takes longer. This is proposed as resulting from the graphitized zone slowing the diffusion of species controlling the longer term corrosion processes. A practical simplified model and its parameters are proposed.

Keywords: A. Iron; B. Weight loss; B. Modelling studies; C: Atmospheric corrosion; C: Pitting corrosion.

1. Introduction

Grey cast iron is the most widely used of the various cast irons. It consists predominantly of iron with 2.5 - 4% C, 1-3% Si and minimal other alloys. The carbon is mainly in the form of graphite, giving grey cast iron its typical grey appearance when fractured [1]. At one time grey cast iron was used widely and extensively for major infrastructure applications such as bridge piers and for water supply pipelines and a considerable legacy of such structures remains. Many of these are in apparently satisfactory condition but structural safety may have been compromised by material loss due to corrosion and by cracking due to high tensile stresses and fatigue. Replacement of major infrastructure usually is expensive, and there is increasing interest in keeping existing structure in-service for longer periods, provided safety and serviceability requirements can be met. Often life extension will be beyond the service life originally intended. If it was predicted at all, expected service life was

estimated at the time of the original design only very poorly, or based on past experience, and based perhaps more on wishful expectation than on sound theoretical bases [2].

For many infrastructure systems interest lies in structural strength. For this the ultimate governing criterion is the probability of structural failure and this is influenced, strongly in most cases, by the remaining average thickness of materials, that is, the material remaining after 'uniform' corrosion [3]. Grey cast iron has favourable long-term corrosion characteristics, particularly in the atmosphere, as witnessed by the existence of many railway bridges in the UK, USA and elsewhere that are over 100 years old. However, grey cast iron can suffer from substantial corrosion in the earlier stages of exposure particularly in seawater, fresh water and in-ground environments [4].

Compared with structural and other steels the quantitative data and information about the corrosion of cast iron is relatively scarce [5,6]. Further, for structural steels, models that describe (and predict) the short- and the longer-term corrosion loss and the maximum pit depth as functions exposure time are available. These include the influence of environmental parameters such as water temperature, water velocity and water quality. This is the case for immersion conditions and to a lesser extent for atmospheric corrosion [7,8].

Since both steels and cast irons consist predominantly of ferric iron with relatively small amounts of alloying, they can be expected to display generally similar corrosion behaviour and trends, even though corrosion losses or pit depths are likely to be different [4]. The analysis below is based on this proposition. Data available in the literature for the corrosion of grey (and some other) cast irons are examined and assessed for trends, using for comparison the bi-modal model earlier shown to be relevant for mild and low alloy steels and for chromium steels under various exposure conditions [9,10]. Both corrosion loss and maximum pit depth are considered. Although the form and the sequential phases of the model have been described previously (e.g. [10]) for reference the key features are shown in Fig. 1.

The division between the two modes is denoted with the parameter t_a . The first mode consists of a very short phase (0) during which corrosion initiates and also, for seawater, the metal surface is colonized by biofilm and then by microorganisms. In phase 1 the rate of corrosion is controlled by the rate of diffusion of oxygen from the water or moisture immediately adjacent to the metal surface ('concentration control') while in phase 2 the corrosion rate is controlled by the rate of oxygen diffusion through the increasing thickness of corrosion products on the metal surface. This produces the characteristic attenuation of the rate of corrosion. Eventually, at around t_a , the rusts have built up sufficiently to develop anoxic conditions over much of the corroding surface. This then provides the

conditions under which aggressive autocatalytic pitting corrosion can occur under the rust products and under which anaerobic microbiological activity also can occur within anoxic niches in the rust layers adjacent to the metal surface [10]. This is phase 3. Phase 4 represents the long-term, probably steady state, corrosion condition.

Figure 1. Bi-modal model for marine corrosion loss (and maximum pit depth) as a function of exposure period. Parameter t_a defines the transition between the modes.

For infrastructure life extension purposes the long-term rate r_s is of primary interest and also the intercept c_s at $t = 0$ on the corrosion loss axis of Fig. 1 [11]. Estimates of r_s can be made by inspection or one or more of a variety of specialised techniques to ascertain corrosion loss or pit depth. Let the outcome of such an inspection be denoted $c(t_i)$ where $0 - t_i$ is the time interval between when the structure was first placed into service and the time of inspection or observation (Fig. 2a). If there had been an earlier time of inspection or observation t_e , say, (Fig. 2b) it is possible to use the respective observations of corrosion loss (or pit depth) to make an estimate of the long-term corrosion rate r_s as $r_s \cdot (c(t_i) - c(t_e)) / (t_i - t_e)$. However, since in many practical situations concerns about corrosion tend to arise relatively suddenly, $c(t_e)$ is seldom measured in practice. Typically only one or some estimates of $c(t_i)$ are available at time t_i and these are insufficient by themselves to estimate r_s and c_s . More information is required.

More information can be brought to the problem if a theoretical model, preferably calibrated to actual field data, is available to describe the expected trend of the corrosion loss (or opt depth) as a function of exposure time. In this ways the underlying corrosion loss trend expected for the particular application can be predicted from past experience and, ideally, relevant theoretical concepts (Fig. 2c). Herein the possibility is explored that the underlying corrosion loss trend (and the trend for maximum pit depth) for grey cast iron is consistent with the bi-modal model (Fig. 1). The approach throughout is to consider whether it is possible for the data reported in the literature to have been generated by an underlying bi-modal distribution of the form of Fig. 1. Conversely, there is no *a priori* assumption that the data fit a power law or any other continuously smooth concave function.

Figure 2(a) Corrosion loss observation $c(t_i)$ at time t_i and the required long-term rate r_s (b) estimation of the long-term rate r_s from two (or more) observations at t_e and t_i respectively and (c) extrapolation based on a known theoretical model. Note that in (a) the ‘apparent corrosion rate’ $c(t_i) / t_i$ gives a misleading (over-)estimate of r_s .

The next section outlines the study approach and reviews all the quantitative data found, after extensive searches, to be available in the literature. This is followed by an examination of the data for grey cast iron and examines possible consistency with the bi-modal model. Data for some other cast irons and cast steel are then considered. In all cases the data either clearly follows a bi-modal trend or can be interpreted as following such a trend. The possible reasons for this behaviour are then discussed and some practical implications outlined.

2. Study methodology and data

The most extensive quantitative observations for the corrosion loss of grey cast iron were obtained in the Panama Canal Zone (PCZ) for marine immersion, mid-tide and two different marine atmospheric exposures and also for fresh water immersion corrosion. The seawater exposures were carried out at Naos Island and the fresh water immersion exposures in Gutan Lake [12,13]. At these two sites the water temperatures averaged 27 and 28°C respectively. Full details are given in the original papers but in summary the seawater was considered typical for open ocean conditions and the Lake water was noted as fairly 'soft' and neutral, averaging 0.1 ppt dissolved solids and pH 7.5. The atmospheric coastal marine zone exposure sites were (i) at Coco Solo (PCZ) at 17m elevation and (ii) about 1.6 km inland from the coast, about 1.5m above ground level.

The coupons in all cases were 230 x 230 x 6 mm in size. The composition of the cast irons and cast steel are shown in Table 1. In the main the coupons were exposed continuously for 1, 2, 4, 8 and 16 years although there are some gaps in the data and in some cases longer exposures were not made. Coupon exposure surfaces were either 'as-cast' or were machined to remove the casting surface layer.

This was done on the basis of previous experience [4] that suggested that the machined surfaces would show more severe pitting corrosion. Table 1 also shows the composition of mild steel exposed at the same locations. It was used together with much other data to calibrate the model Fig. 1 [9] and is used below for comparison purposes.

Table 1. Composition (% by weight) for corrosion tests of cast irons and for cast steel [12].

Description	Specification	C	Mn	P	S	Si	Cr	Ni	Cu
Grey Cast Iron	QQ-I-652, 30	3.18	0.80	0.162	0.103	1.98	0.57	0.31	0.08
Cast Steel	QQ-S-6816, 1	0.27	0.68	0.028	0.028	0.41	0.12	0.22	0.10
Austenitic Cast Iron	INCO 18-22 Ni	2.66	0.94	0.24	0.104	3.17	2.29	17.9	0.80
Mild (Carbon) Steel	QQ-S-741 IIA1	0.24	0.48	0.04	0.027	0.008	0.03	0.051	0.08

Details of the exposure programme and the experimental techniques are given in the original references. Herein only the corrosion loss values obtained (as average values from duplicate coupons) in the experimental programme are of interest. In all cases the reported corrosion loss values have been converted to metric units and are plotted without correction (except as noted). The corrosion loss trends originally reported have not been used. Instead, new trends that are generally consistent with the data have been added. In the Figures that follow, the lighter continuous lines are lines of best fit obtained using a standard smooth curve fitting routine employing the Stineman smoothing function [14]. Also shown in some cases are bold 'interpreted' trends. These are drawn subjectively, anchored at the data points (i.e. the reported observations) and using the expectation that the underlying data trends should be generally consistent with one another.

The analysis technique employed herein is as follows. Since steels and cast irons consist essentially and predominantly of ferric iron with small proportions of alloying, it is reasonable to expect that they would display generally similar behaviour and trends, although not necessarily quantitatively similar corrosion losses or pit depths [4]. Specifically, the data available in the literature for the corrosion of grey (and some other) cast irons (and steels) are re-examined and also assessed for trends, using for comparison the bi-modal model (Fig. 1) shown earlier to be relevant for mild and low alloy steels and for chromium steels under various exposure conditions [15]. For reference in the following, Figs. 3 and 4 show the typical corrosion loss - exposure time functions obtained previously for mild steel for each of the Panama Canal Zone (PCZ) exposure environments [9, 15]. The values of t_a (see Fig. 1) are summarized in Table 2.

Table 2. Typical value of model parameter t_a for mild steel in different exposure environments at 27°C.

Environment	Marine Immersion	Marine Mid-tide	Marine Coastal Atmospheric	Marine Inland Atmospheric	Fresh Water Immersion
Value of t_a (years)	0.7-0.8	3	4.5	6	5-6

Figure 3. Corrosion loss – exposure time plots for mild steel in various marine exposure environments. Data from [12, 13]. Trends are interpreted for immersion and for inland atmospheric corrosion and are shown in bold (coloured) lines.

Figure 4. Corrosion loss – exposure time plots for mild steel in freshwater. Data from [12, 13].

3. Grey Cast Iron

Under marine immersion and tidal conditions Fig. 5 shows the corrosion losses for machined and for ‘as-received’ surfaces for coupons. The ‘as-received’ will be taken throughout as equivalent to ‘as-cast’ surface finish. It is clear that the data needed only a small amount of interpretation to obtain the trends shown through the data points. The corrosion losses for the grey cast iron with ‘as-received’ surface finish are much lower than those for the machined surfaces, at least for the 4 years during

which the tests were carried out. For the machined surfaces the corrosion losses are high compared with those for mild steel (Fig. 3) and the time t_a much longer.

Figure 5. Grey cast iron corrosion losses for immersion and for mid-tide exposures in the PCZ and trends through the data, showing also the difference in corrosion losses between machined and ‘as-cast’ surfaces (Data from Southwell and Alexander [12]).

Fig. 6 shows the corrosion loss trends for fresh water immersion, again for machined and for ‘as-received’ surfaces for coupons. In this case the time t_a is comparable to that shown in Fig. 4 for mild steel in fresh water. Also the corrosion losses are similar to those for mild steel.

Figure 6. Cast iron corrosion losses for coupons exposed to fresh water immersion in Gutan Lake, PCZ and fitted trends, showing only a small difference in corrosion between machined and ‘as-cast’ surfaces (Data from Southwell et al. [13]).

For atmospheric exposures, Southwell et al. [12] provide data for summarized in Fig. 7a for grey cast iron coupons (machined and ‘as-received’). There is no clear evidence of a bi-modal trend in this interpretation in part because of the lack of data in Fig. 7 between years 4 and 8. However, invoking the notion of consistency, and the fact that both atmospheric corrosion trends for mild steel in Fig. 3 show a modest bi-modal character, it is possible that there is an underlying bi-modal trend also in the data in Fig. 7, as shown in slightly exaggerated form in Fig. 7b.

Figure 7. Corrosion loss data for machined grey cast iron for coastal and inland exposures in the PCZ showing data points with (a) best fit curves fitted through the data, and (b) with subjectively fitted and possibly exaggerated bi-modal trends (shown with thick lines). (Data from Southwell et al. [13]).

The only other set of long-term data for grey cast iron is summarized by McCaul and Goldspiel [16], given in their Figure 30.4 and replotted here in Fig. 8. The data is for exposures at Kure Beach, NC at the 80foot (25m) site, recorded over a period of 15 years. It is clear that the data trends are consistent with bi-modal corrosion behaviour. Closer examination showed that the reported corrosion losses are much higher than normally be expected for marine atmospheric exposure conditions. The original source for these data could not be traced from the information supplied in [16]. Fig. 8 has been plotted on the basis that, compared to other data sources for atmospheric corrosion at Kure Beach, the reported data values appear to be about one order of magnitude too high. Of course this has no effect on the bi-modal characteristic of the data set.

Figure 8. Corrosion loss data and best fit trends for grey cast iron as machined and as-cast, exposed at Kure Beach NC in marine atmosphere (data corrected from McCaul and Goldspiel [16]).

Data for maximum pit depth on grey cast iron are scarce, despite some being reported by Southwell and Alexander [12] and Southwell et al. [13]. In many cases the coupons were pitted through after 8 years for immersion conditions and sooner for tidal conditions, despite the accepted conventional wisdom is that grey cast iron pits relatively slightly but somewhat more than most other cast irons [4]. The total depth of pitting measured from the original surface and thus including the ‘general’ corrosion losses are shown in Figure 9 for immersion exposures in the PCZ.

Figure 9. Mean total pit depth (average of 20 deepest pits on duplicate coupons) for machined grey cast iron continuously immersed in seawater in the PCZ, together with isolated observations reported for maximum total pit depth (Data from Southwell and Alexander [12]).

4. Some other cast irons and a cast steel

Some longer-term corrosion data are available in the literature for cast steel and for austenitic cast iron (Table 1), although again it is limited. Fig. 10 shows data for cast steel as reported by Southwell and Alexander [12] but with the reported data at 16 years interchanged between immersion and mid-tide corrosion, based on the expectation of consistency with all the other data reported by these authors for immersion and tidal exposure corrosion losses. Their data shows that the trends for years 4 to 16 for mild steel, 2 nickel-rich steels, 2 chromium-rich steels, 4 low-alloy steels, 2 wrought irons as well as for grey cast iron and austenitic cast iron, all have the immersion losses at 16 years greater than those for the tidal zone. It is therefore unlikely that this is not the case also for cast iron. In practice it is not impossible to have a mix-up of coupons from the two exposure sites at 16 years. However, irrespective of this adjustment, it is clear from Fig. 10 that there is a inflexion in the corrosion loss trend at around 2.5-3 years exposure for all four trends – for machined and for ‘as-received’ coupons and for both immersion and mean tide exposures, irrespective of the corrosion losses at 16 years exposure.

Figure 10. Cast steel corrosion loss data and best fit trends for immersion and mid-tide exposures in the PCZ and trends, including machined and as-cast cast surface finishes (a) with data taken directly from Southwell and Alexander [12] and (b) with data at 16 years inter-changed (see text).

Fig. 11 shows the corrosion data and the best fit trends for cast steel in fresh water. Fig. 12 shows the corrosion loss data and the trends for austenitic cast iron in tidal and marine immersion exposures. The data for the ‘as-received’ coupons is limited to just 2 years exposure before pitting penetrated the coupon and rendered mass loss results meaningless. Figs. 13 and 14 shows coastal zone atmospheric corrosion data and trends for cast steel and for austenitic cast iron, respectively, in each case compared with grey cast iron.

Figure 11. Cast steel corrosion loss data for fresh water immersion exposure in Gutan Lake, PCZ and fitted trends (data from Southwell et al. [13]).

Figure 12. (a) Data for corrosion losses for austenitic cast steel for immersion and for mid-tide exposures in the PCZ and (b) interpreted trends (data from Southwell and Alexander [12]).

Figure 13. (a) Atmospheric corrosion loss data and best fit trends for machined cast steel (b) with same data as in (a) but showing interpreted trends (data from Southwell et al. [13]).

Figure 14. Atmospheric corrosion loss data and trends for machined austenitic cast iron and machined grey cast iron (Fig. 5) with interpreted trends for the cast steel data (data from Southwell et al. [13]).

5. Discussion

In the approach used herein the data available from all sources quoted are viewed in the first instance as sets of samples generated by underlying (physical-chemical) processes. These samples provide information about the outcome of the state of the underlying processes at the time the sampling was done but say nothing about the state(s) any other time or about the transition from one state to the next.

Thus, for the PCZ experiments, all sampling was done at 1, 2, 4, 8 and 16 years and the observations at these times are, for the present study, the only outcomes (value data set) that are taken as ‘fixed’. In principle any potential model for the underlying process(es) to describe the evolution from one state to the next in the data set should be consistent with this data set. However, at all other time points the function can take whatever form can be justified from theoretical and practical considerations. One such function (model) is the celebrated power-law [17,18] described (for corrosion loss) by $c(t) = A t^B$ where A and B are constants obtained from fitting the function to data and t is the exposure period. As shown previously for steels, the power law does not deal with data sets as well as does the bi-modal model [7,8,9,11,15] for reasons discussed previously [10]. In contrast, the data sets considered in Figs. 5-14 above show consistency with the bi-modal model. The interpretation used shows that the bi-modal can be fitted to data sets for marine immersion and tidal corrosion and fresh water immersion corrosion of grey cast iron, cast steel and austenitic cast iron (Table 1). The data for marine atmospheric corrosion also can be interpreted as consistent with the model, particularly when viewed in the context of earlier work on marine atmospheric corrosion of steels [19].

It is acknowledged that the bi-modal form is functionally more complex than the power law and that it requires more parameters to fully characterize it mathematically (e.g. Fig. 1). More data also is required to provide quantitative calibration of the model to field data. For steels in immersion conditions this largely has been achieved but for cast irons it is clear that more data, particularly long-term exposure data is required for calibration to be done. Extending the data-base through the conduct of long-term field trials clearly is not a trivial task because of the long time horizons involved and the required commitment of resources and staff. Also, it would be many years before useful results became available. It is considered that a more practical approach is for existing cast iron structures to be examined in-situ to ascertain corrosion losses through measurement of the thickness of the graphitized layer and correlating this to the likely historical environment and the exposure period. Such work is currently in progress for cast iron bridge piers around 100 years old exposed to a tropical marine environment. The outcomes will be reported in due course. With the availability of such data also from other sources, model calibration will become possible.

A more theoretical question is how the corrosion of cast iron can develop a bi-modal trend (Fig. 1) for corrosion loss and for pit depth in parallel to that observed previously for the corrosion of steel. The similarity suggests that parallels exist between the mechanisms involved in the corrosion of steels and the corrosion of cast iron and that these result largely from the build-up of corrosion products. In Fig. 1 corrosion is rate-controlled in phase 2 by rate of diffusion of oxygen from the external environment through the corrosion products to the corroding surface. As the corrosion products build-up the corrosion rate declines. This applies both for general corrosion and for pitting, leaving, in general,

variations in the topography of the corroding metal surface. This surface may be characterized as a non-uniform, non-homogeneous, spatially varying surface with corresponding non-uniform and non-homogeneous corrosion product layers [20]. As a result spatial differences can be expected in the development of localized low oxygen or anoxic conditions on the corrosion interface. These localized differences will cause differences in potential and in pH and in initiation of localized corrosion or pitting, consistent with the theory of differential aeration [17]. These conditions also will permit commencement of highly aggressive autocatalytic crevice corrosion and pitting under anoxic conditions [21, 22, 23]. In the context of Fig. 1, this corresponds to the commencement of phase 3. A similar scenario is possible for the corrosion of the cast irons and steel. For grey cast iron in particular the loss of iron content in the outer zones leaves behind a skeleton of graphite flakes (the 'graphitized' zone) [17, 24, 25]. The graphite flakes have been proposed as contributing to corrosion through being cathodic to the iron matrix [4], causing iron dissolution and permitting ferrous ion migration but this cannot explain the bi-modal characteristic. Similar to the case for steel corrosion, it is more likely that the aggressive corrosion at the commencement of phase 3 is the result of the development of anoxic regions resulting from the oxidation products forming within the graphitized layer permitting localized highly aggressive autocatalytic crevice corrosion and pitting.

As for steel, the anoxic regions in principle also could permit the development of bacterial corrosion provided the local environmental conditions are appropriate and provided nutrients are available [26]. Indeed, the accelerated corrosion of cast iron has been attributed to the activity of bacteria, particularly the sulfate reducing bacteria [e.g. 27]. However, these deductions are based largely on the presence of bacteria having been observed rather than on direct measurement of their contribution to corrosion. The actual contribution of bacteria to the marine corrosion of cast iron remains a matter for more detailed investigation.

Under long-term exposure conditions, that is, in phase 4 of the model of Fig. 1, the rate of corrosion is likely to be controlled by a slow diffusion mechanism. Candidate possibilities include (i) inward diffusion of water towards the corroding surface, (ii) outward diffusion of hydrogen produced by anoxic crevice corrosion and (iii) outward diffusion of ferrous ions, in each case through the rust-filled graphitized zone. While (ii) may control early in phase 3, this cannot continue for very long owing to the much greater molecular sizes of the other species and the reducing diffusivity (and thickness) of the graphitized zone as corrosion continues. It is likely that the eventual rate-controlling step will be the outward diffusion of ferrous ions through the graphitized layer, a mechanism first proposed by LaQue [4]. This layer is likely to be much less permeable than the rusts typically formed on the outside of steels and on cast irons and would account for the very low rate of long-term corrosion typical of cast irons [4], machined or otherwise, even if the earlier corrosion is more severe (Figs. 3 and 5).

Although this mechanism is plausible, direct experimental evidence does not appear to be available at the present time. Long-term studies and detailed investigations of the electro- and physical chemistry involved will be required. As noted above, this will require a major financial and experimental commitment to well-instrumented field studies. For obvious reasons, laboratory studies are unlikely to be practical. At this time a more realistic approach may be simply to accept that complete understanding of the mechanics involved remains an open question.

Comparing the data and trends for immersion and for mid-tide corrosion for mild steel shown in Fig. 3 with those for cast steel in Fig. 10 shows that the corrosion behaviour of machined cast steel is generally consistent with that of the mild steel. This is likely to be the result of these materials having similar compositions (Table 1). It suggests that the differences in the outer grain structures of steel and iron [28] are not very important in governing corrosion behaviour at this scale.

Comparison of corrosion losses in the tidal and the immersion zone shows that for cast iron the former are higher, at least for the early exposure period but not for longer exposure periods (Fig. 5). For cast steel, however, the tidal corrosion losses apparently are lower throughout (Fig. 10). This suggests the importance of the relative contribution of the diffusion characteristics and the protection offered by the rusts and other deposits in the graphite matrix layer, first for oxygen diffusion and later for hydrogen and ferrous ion diffusion. This aspect also warrants further investigation. It is anticipated that the current study (see above) of the corrosion of cast iron bridge piers exposed for some 100 years to marine atmospheric, tidal and immersion conditions will throw some light on this issue.

The effect of salinity can be seen by comparing the corrosion losses in Fig. 5 and 6. For cast iron continually immersed in seawater Fig. 5 shows that the trend curve is, for the first 4 years or so, slightly higher than in fresh water (Fig. 6) and thereafter the difference becomes larger. Similar differences in corrosion loss trend can be seen for the austenitic cast iron and for cast steel (Figs. 10 and 11). Hence the difference is unlikely to be a function of material composition, consistent with corrosion controlled by diffusion being insensitive to the precise metal composition [17] provided there is not a high degree of alloying (such as for ferritic or Ni rich cast irons). Also, large differences have not been associated with salinity for mild steel in fresh, brackish and seawater immersion corrosion [15]. This indicates that the results shown in Figs. 5 and 6 require further investigation, perhaps using a historical study of existing cast iron structures exposed in different salinity environments (see above).

The practical outcome of the interpretations given above is that the longer term corrosion rate r_s (Figs. 1 and 2) is somewhat less than the average corrosion rate (Fig. 2a). As noted, the value of r_s is of

particular interest in estimating the likely future rate of corrosion for infrastructure that has already corroded and has been inspected and assessed (at t_i) (Fig. 2a). More generally the parameter c_s also is of interest. Tables 3 and 4 give a summary of values of c_s and r_s respectively estimated directly from Figs. 5-14. For comparison, for mild and low alloy steels c_s values are around 0.1mm and r_s typically is in the range 0.05-0.07mm/y [29].

For mild and low alloy steels r_s is relatively insensitive to water temperature [29]. Since the corrosion behaviours of cast irons and cast steel have been shown herein to be similar to those of mild and low alloy steels, similar insensitive to water temperature can be expected. However, this also remains an area for further investigation. For cast iron exposed to marine environments the historical study currently in progress for 100 year old bridge piers (see above) is expected to assist in the estimation of c_s and r_s . However a more comprehensive analysis will require similar studies in non-marine environments.

Table 3. Estimated longer-term corrosion intercept c_s (mm) at PCZ sites for machined surfaces.

Exposure Condition	Fresh water		Seawater Immersion		Tidal		Atmosphere coastal		inland
Grey Cast Iron	0.45	(6)	0.075-0.1	(5)	0.5	(5)	0.09	0.06	(7, 8)
Cast Steel	0.35	(11)	0.25-.3	(10)			0.08	0.04	(13)
Austenitic Cast Iron			0.25	(12)	~ 0.0	(12)	~ 0.07	~ 0.0	(14)

Note: Numbers in brackets () refer to the Figures from which the rates were estimated.

Table 4. Estimated longer-term corrosion rates r_s (mm/y) at PCZ sites for machined surfaces.

Exposure Condition	Freshwater		Seawater Immersion		Tidal		Atmosphere coastal		inland
Grey Cast Iron	0.03	(6)	0.1	(5)	0.1	(5)	0.006 – 0.007	0.06	(7, 8)
Cast Steel	0.02	(11)	0.04	(10)			0.01	0.04	(13)
Austenitic Cast Iron			0.023	(12)	~ 0.015	(12)	~ 0.005	~ 0.07	(14)

Note: Numbers in brackets () refer to the Figures from which the rates were estimated.

The data reviewed herein and the trends derived from the data support the hypothesis that cast irons and cast steels follow a bi-modal trend for corrosion loss (and also pit depth) with increased exposure period. In principle, additional supportive field data could strengthen the hypothesis. However, it is considered that there is sufficient support at this time since the data available already cover a wide range of realistic exposure conditions.

The observation that the bi-modal model differentiates into a number of sequential phases opens up the possibility that each of these could be investigated separately. This represents a complete break with

tradition, and means that laboratory studies could be used to clarify mechanisms currently not fully understood, particularly those in phases 3 and 4 of the model. Of course, the field conditions would need to be replicated adequately.

4. Conclusions

1. Literature data for the long-term corrosion of grey cast iron, austenitic cast iron and cast steel exposed to marine, fresh-water and atmospheric environments as a function of time is consistent with the bi-modal relationship previously observed for mild and low alloy steels. Compared to immersion and tidal exposures the bi-modal characteristic is less pronounced for atmospheric exposure conditions. The corrosion trends are not consistent with the classical power law typically used for long-term corrosion trends and prediction.
2. The long-term rate of corrosion of machined cast irons is about 10% of that for mild and low alloy steels. This is considered to be the result of the graphitized layer holding protective corrosion products more effectively and thus providing a more effective diffusion barrier than is the case for the rusts that form on the exterior surfaces of cast steel and for mild steel.
3. Over the period of 4 years exposure for which data are available, the corrosion losses for machined cast iron surfaces are about twice as high as for as-cast surfaces. Since the cast irons were otherwise identical, this result must be attributed to the dense outer skin of as cast surfaces.
4. It is proposed that the early part of the second mode in the bi-modal functional relationship is the result of the formation of localized anoxic niches under the graphite matrix layer that then facilitate highly aggressive autocatalytic crevice and pitting corrosion. The extent to which the localized anoxic niches permit localized anaerobic bacterial activity and microbiological corrosion remains an area for further investigation.

Acknowledgements

The financial support of the Australian Research Council is acknowledged.

References

- [1] H.T. Angus, Cast Iron: Physical and Engineering Properties, Second Edition, Butterworths, London, 1976.

- [2] J. Heyman, Elements of the theory of structures, Cambridge: Cambridge University Press, 1996.
- [3] R.E. Melchers, The effect of corrosion on the structural reliability of steel offshore structures, Corros. Sci. 47(2005) (10) 2391-2410.
- [4] F.L. LaQue, The corrosion resistance of ductile irons, Corrosion, 14(1958) 485t-492t.
- [5] M. Schumacher (Ed.), Seawater Corrosion Handbook, Park Ridge, New Jersey; Noyes Data Corporation, 1979.
- [6] G. Kreysa, R. Eckermann, Dechema Corrosion Handbook, Vol 11, VCH Publishers, New York, 1992.
- [7] R.E. Melchers, Development of new applied models for steel corrosion in marine applications including shipping, Ships and Offshore Structures 3(2008) (2) 135-144.
- [8] R.E. Melchers, Long-term corrosion of steels exposed to marine environments, European Journal of Environmental and Civil Engineering, 13(2009) (5) 527-546.
- [9] R.E. Melchers, Modeling of marine immersion corrosion for mild and low alloy steels - Part 1: Phenomenological model, Corrosion, 59(4) (2003) 319-334.
- [10] R.E. Melchers, 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.
- [11] R.E. Melchers, Experiments, Science and Intuition in the development of models for the corrosion of infrastructure, Proc. Corrosion & Protection, Coffs Harbour, Australasian Corr. Assn., Melbourne, 2009.
- [12] C.R. Southwell, A.L. Alexander, Corrosion of metals in tropical seawaters: Structural Ferrous metals, Materials Protection, Jan (1970) 14-23.
- [13] C.R. Southwell, J.D. Bultman, A.L. Alexander, Corrosion of metals in tropical environments - Final report of 16-year exposures, Materials Performance, 15(1976) (7) 9-25.
- [14] R. W. Stineman, A consistently well-behaved method of interpolation. Creative Computing, July 1980.
- [15] R.E. Melchers, Modelling immersion corrosion of structural steels in natural fresh and brackish waters, Corros. Sci. 48(2006) (12) 4174-4201.
- [16] C. McCaul and S. Goldspiel, Atmospheric corrosion of malleable and cast irons and steels, (In) Atmospheric Corrosion (Ed.) W.H. Ailor, Wiley-Interscience, New York, 1982.
- [17] U.R. Evans, The corrosion and oxidation of metals: scientific principles and practical applications, London: Edward Arnold (Publishers), 1960.
- [18] M. Pourbaix, The linear bilogarithmic law for atmospheric corrosion, (In) Atmospheric Corrosion, (Ed.) W.H. Ailor, New York: John Wiley and Sons, 1982, 107-122.

- [19] R.E. Melchers, The transition from marine immersion to coastal atmospheric corrosion for structural steels, *Corrosion*, 63(2007) 500-514.
- [20] K. Asami, M. Kikuchi, In-depth distribution of rusts on a plain carbon steel and weathering steels exposed to coastal-industrial atmosphere for 17 years, *Corros. Sci.* 45(2003) 2671-2688.
- [21] G. Wranglen, Active sulphides and the pitting corrosion of carbon steels, (In) *Localized Corrosion*, Proc. Conf. Dec. 6-10, Williamsburg, VA, NACE Publication No. 3, National Association of Corrosion Engineers, Houston, TX, (1974) 462-476.
- [22] A. Turnbull, Review of modelling of pit propagation kinetics, *British Corrosion Journal*, 28(1993) (4) 297-308.
- [23] L.L. Shreir, Localised corrosion, (In) *Corrosion*, Vol. 1, (3rd Edn.), (Ed) L.L. Shrier, R.A. Jarman and G.T. Burstein, Oxford: Butterworth-Heinemann (1994) 1:151-1:212.
- [24] Y.S. Shepelev and L.F. Rudenko, Mechanism of gray cast iron corrosion, *Materials Science*. 14(1976) (1) 86-87.
- [25] L.L. Shreir, R.A. Barman, G.T. Burstein (Eds.), *Corrosion*, Butterworth-Heinemann, Oxford, UK, 3rd edition (1994).
- [26] W.A. Hamilton, Sulphate-reducing bacteria and anaerobic corrosion, *Ann. Rev. Microbiol.* 39 (1985) 195-217.
- [27] K.R. Butlin, Sulphate-reducing bacteria and internal corrosion of ferrous pipes conveying water, *Nature* 163 (1949): 26-27.
- [28] F. Vander Voort, Microstructure (Chapter One) (In) *Metallography: Principles and Practice*, ASM International, 1984.
- [29] R.E. Melchers, Modeling of marine immersion corrosion for mild and low alloy steels - Part 1: Phenomenological model, *Corrosion* 59(2003)(4) 319-334.

1. longer term corrosion of various cast irons shows a bi-modal trend with exposure time
2. this applies for marine immersion, tidal and freshwater and for atmospheric corrosion
3. proposed as resulting from pitting under anoxic conditions under corrosion products