NOVA

University of Newcastle Research Online

nova.newcastle.edu.au

Melchers, R. E. "Bi-modal trend in the long-term corrosion of aluminium alloys" Corrosion Science Vol. 82, p. 239-247 (2014)

Available from: <http://dx.doi.org/10.1016/j.corsci.2014.01.019>

Accessed from: <http://hdl.handle.net/1959.13/1054928>

Bi-modal trend in the long-term corrosion of aluminium alloys

Robert E Melchers*

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

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

Abstract

A wide range of literature data including in-situ immersion, tidal, coastal atmospheric and industrial exposures is used to show that the trend for longer term corrosion of aluminium alloys is nearly always more consistent with a bi-modal model than with the classical power-law function. It is proposed the bi-modal characteristic results from the accumulation of corrosion products causing localised anoxic conditions. These permit a change from predominantly cathodic oxygen reduction to hydrogen ion reduction under anoxic autocatalytic conditions within pits. This mechanism is consistent with established theory for pitting corrosion in aluminium.

Keywords: A: Aluminium; B: Modelling studies; C: Atmospheric corrosion; C: microbiological corrosion.

1. Introduction

Aluminium and aluminium alloys generally display very favourable corrosion resistance, showing little general and very moderate pitting corrosion, even in marine exposure conditions [1,2,3]. These characteristics have made aluminium and its alloys of particular interest in aerospace, defence and marine applications and increasingly in structural and other commercial infrastructure. In many cases longer-term durability without protective coatings and with minimal maintenance is an important performance requirement. In turn this requires an ability to predict the likely long-term corrosion loss, material strength loss or maximum pitting depth as a function of exposure time. Since the design of major infrastructure invariably employs analytical mathematical or numerical engineering models derived from experience, observation and data, analytical models also are desirable for the prediction of long-term corrosion. Ideally such models are based on reasonably accurate representations of field data and on a recognition of the most important factors and mechanisms involved. The need to develop such models or trends for the long-term corrosion of aluminium and aluminium alloys motivates the present work.

It is well known that aluminium develops a thin protective oxide film when exposed at ambient temperatures to environments containing oxygen [4]. Usually the associated mass-loss is very small. Corrosion tends to be non-uniform over the metal surface and conventional measures of corrosion, including mass loss and maximum pit depth, are likely to be difficult to obtain accurately and may show considerable variability. For these reasons other measures such as average pit depth or average loss of tensile strength have been used in some studies. Herein the data as reported in the original source material is employed.

For aluminium and aluminium alloys a number of studies have reported the development of corrosion with time, mostly for short-term observation periods. A useful summary has been given Szklarska-Smialowska [4]. Mostly the exposures are for hours, days or weeks. There are only a few data sets for long-term exposures. These include the 20 year data for a variety of environments in the USA [5], the 16 year study of aluminium pitting and mass loss in marine environments in the Panama Canal Zone [6], the 7 year data for in-land atmospheric corrosion, also in the USA [7], the 10 year observations for various atmospheric exposure conditions in Sweden [8] and the 30 year observations of atmospheric corrosion in mainland USA [9]. The data from these laboratory studies and empirical field studies mostly have interpreted the data in terms of the well-known and widely applied power-law function for the corrosion of metals as a function of time:

$$c(t) = At^B \quad (1)$$

with c is corrosion loss or pit depth, t is exposure time and A and B are constants obtained from fitting the function to data.

There is also a 10-year study of a number of aluminium alloys exposed to atmospheric conditions on the Spanish Mediterranean coast [10]. This study interpreted the relationship between mass-loss c and exposure time t as approximately linear. Also, for maximum pit depth and for the average of the 15 deepest pits, the following empirical semi-log relationship was proposed:

$$c_p(t) = a + b \log t \quad (2)$$

where $c_p(t)$ is the maximum or average pit depth, t is exposure time and where a and b are constants obtained from fitting the function to the observations.

The mathematics for Eqn. (1) and the resulting simplified format were derived originally in 1923 by Tammann [11] for the inland atmospheric corrosion of copper. It is based on the mathematics of

the diffusion of oxygen through the increasing thickness of the copper corrosion product layer that forms on the surface as the copper corrodes. Eqn. (1) has been used widely as an empirical fit to data sets reported in many corrosion studies for many different metals. Pourbaix [12] notes that Passano did so already in 1934, apparently without reference to the original theory. The theory has since been refined [13,14] and it has been shown that when applied to the marine immersion corrosion of steel Eqn. (1) is more consistent if considered not to apply immediately from first exposure and is limited to relatively short exposure periods [15]. This then avoids the considerable variations in the constant A and in the exponent B found in some studies, for example when Eqn. (1) was applied for several years of exposure of steels in marine environments [16,17].

Similar instability in A and B has been reported when Eqn. (1) is applied to the longer term corrosion of aluminium. For example, for various grades aluminium and aluminium alloys exposed to inland US conditions for exposure periods up to 30 years, Sowinski and Sprowls [9] found B to range from 0.33 to 1.0 or more. However, for exposures up to 16 years at a number of Spanish atmospheric sites Eqn. (1) was considered entirely appropriate to represent the progression of corrosion loss [18]. Similarly, [de la Fuente](#) et al. [19] in an extensive review of many of the available data, including that for short exposure periods, concluded that Eqn. (1) is the most appropriate function for longer-term exposures. Further, a recent study of 10- and 20-year observations for mass loss obtained in mainland China concluded that Eqn. (1) correlated well with the reported data [20].

In most of these cases analytical support for the judgement that Eqn. (1) provides a sufficiently good fit to the data was based on plotting the data on a log-log plot. On such a plot Eqn. (1) is a straight line and data consistent with it closely follows that line. However, a log-log plot also tends to make deviations from Eqn. (1) much less obvious when visually compared to the same data represented on a natural axes plot.

The next section of this paper demonstrates that the data sets published in the open literature for longer-term corrosion of aluminium when plotted on plots with natural axes in most cases do not show good agreement with Eqn. (1). Instead, most data show trends that are much more consistent with the bi-modal form (Fig. 1) previously proposed for the corrosion of steel [21,22]. In examining the trends in the data for aluminium corrosion, marine immersion, marine tidal and fresh water immersion are considered as well as a small number of cases of atmospheric corrosion. The subsequent section explores the reasons for the bi-modal corrosion characteristic for aluminium. It is proposed that it is the result of the build-up of corrosion products reducing the diffusion of oxygen to the corroding surface and thus also to any areas of localized corrosion (pitting). This is

considered to create conditions suitable for localized differential aeration and pitting (and possibly crevice corrosion) under areas with localized anoxic conditions, consistent with previously presented concepts for fast pit growth under autocatalytic hydrogen ion reduction and reducing pH within the pits [23, 24], followed by slow long-term polarization. Some consideration is given also to the possibility that microbiologically influenced corrosion may be involved.

Figure 1 here

2. Data and interpreted data trends

2.1 Marine immersion

Figs. 2 and 3 show data sets for aluminium Al 1100 and Al 6061-T respectively exposed for 16 years to fresh water immersion and to seawater immersion and mid-tide conditions in the Panama Canal Zone (PCZ) [6]. In each case the data in the set show a gradual decline in the rate of increase of corrosion loss for the first few years followed by an increase after about 6 years of exposure. This pattern is obviously inconsistent with the power law Eqn. (1). Trend lines (light) have been drawn through the data using a standard smooth curve fitting routine employing the Stineman smoothing function [25]. These trends generally are consistent with the bi-modal trend (Fig. 1). The bold lines are termed ‘interpreted’ trends. They are drawn subjectively but anchored at the data points (i.e. the reported observations), using the expectation that the underlying data trends generally should be consistent with one another and with a bi-modal trend curve. It is seen that in most cases little or no interpretation of the data is required to draw a bi-modal trend curve.

Figure 2 here

Figure 3 here

2.2 Fresh water immersion

Data for freshwater corrosion was obtained in Gutan Lake as part of the extensive long-term corrosion project conducted in the Panama Canal Zone [6]. Fig. 4 shows that the corrosion losses are high, consistent with the low water hardness of the lake waters. The trends in the data for both grades of aluminium do not follow the power law. The trends obtained with the smooth curve fitting routine [25] are not very obviously bi-modal but they could be interpreted as such, as shown, somewhat exaggerated, by the bold interpreted trend lines.

Figure 4 here

2.3 Atmospheric exposures

For a variety of aluminium alloys, Fig. 5 shows data for loss of tensile strength as a measure of atmospheric corrosion over a 20-year period at La Jolla, CA [26]. In two of the data sets there appears to be inconsistency at year 6 since both antecedent and subsequent corrosion (at years 3 and 10) are shown as very much lower. The reason(s) for this type of observation cannot now be ascertained, although it is likely that this type of inconsistency may occur more often for data sets with low overall levels of corrosion. Consideration of all 4 sets of data and working on the expectation of consistency between them leads to the interpreted curves shown, even though this means that one point (marked) needs to be adjusted to half its reported value.

Irrespective of the above issue with some of the data, it is clear that none of the 4 data sets in Fig. 5 is consistent with the power law (Eqn. 1). Instead, the data for Al-1100 shows clear bi-modal characteristics and, with the one adjusted data point, the data sets for the other three cases can be interpreted as bi-modal in each case, as shown.

Figure 5 here

Figs. 6 and 7 show average corrosion loss data for unspecified aluminium alloy for exposure periods up to 5 years for 6 different sites in India [27]. Those in Fig. 6 are for tropical coastal atmospheric marine conditions. Those in Fig. 7 are for industrial atmospheres and show very low corrosion losses. Despite the considerable differences in the corrosion losses only the data set for Cuddalore (Fig. 6) is possibly consistent with the power law (Eqn. 1). The others are very clearly not and can be interpreted easily as bi-modal. This is despite the relatively short overall exposure period. Some data sets have been interpreted as showing a delayed start to the commencement of noticeable corrosion loss. This is not atypical for situations with either low moisture or relatively low temperatures or both immediately after first exposure [2] but does not influence the above observations.

Figure 6 here

Figure 7 here

Data and trends for maximum pit depth of 3 grades of aluminium exposed for 10 years in a cold climate [in Sweden](#) [8] are shown in Figs. 8 and 9. In each case the bi-modal trend is evident, although it is much slower to develop for the industrial atmosphere compared with the marine atmosphere.

Figure 8 here

Figure 9 here

Data for two warm weather coastal sites in Argentina were reported as corrosion rates [28] and have been converted to average corrosion losses. They are shown in Fig. 10. The trends in the data clearly are not consistent with the power law. However, only the data for [Camet](#) has a clear bi-modal functional form. The data and best fit trend (light broken curve) for [Jubany](#) are contradictory. Corrosion is a non-reversible process so that in principle corrosion losses for longer exposures cannot be lower than those for shorter exposures. It is unlikely that natural variability in corrosion could have produced the inconsistencies shown. At [Jubany](#) the chloride deposition rates for the first 2 years were very much lower (about 20%) than subsequently (when it was about the same as at [Camet](#)), and rainfall was not recorded for years 1-3, although relative humidity was very similar throughout and similar to that at [Camet](#) [28]. These weather inconsistencies also are unlikely to have produced the data for the trend at [Jubany](#). It is possible for errors in observation, in transcription, in mass loss estimation and in the determination of the corrosion rates as reported but it is not now possible make any determination. Two possibilities for interpreted trends are shown, assuming that the data at years 1 and 4 are correct. Of these, the [bi-modal](#) function may be considered more plausible [for either interpretation](#).

Figure 10. here

Fig. 11 shows data sets for marine-urban exposures and industrial-urban exposures in Russia over a 10-year period [29]. In both cases the data displays clear bi-modal characteristics. No interpretation is required. Similarly, for aluminium alloys 2024 and 7075 [20] Figs. 12 and 13 both [with data obtained in China](#), show that the data are not consistent with the power law but are consistent with bi-modal behaviour.

Figure 11 here

Figure 12 here

Figure 13 here

Finally, Figs. 14 and 15 show average mass loss data for 99% pure aluminium exposed for up to 16 years to severe marine, mild marine, industrial, rural and urban atmospheres in Spain [19]. For these five data sets a weighted curve fit routine with a low level of smoothing [30] produces the bi-modal trends shown. Previously, for the same test sites Morcillo et al. [18] had noted that mass loss data for the corrosion of steel, when plotted on log-log paper, showed two distinct non-overlapping trends. This is contrary to the single trend that would be observed if the data were consistent with the conventional power-law (Eqn. 1). To ascertain whether this is also the case for aluminium, data in Fig. 15 is plotted on the log-log plot shown in Fig. 16. Clearly, it is possible for a single trend line such as AB and CD (light broken lines) to be fitted through all the data but it is not a good fit. Two distinct lines (shown in bold), one for each part of the data, provide a much better fit. This is mathematically consistent with the bi-modal trends shown in Fig. 15. It is also consistent with the observations by Morcillo et al. [18] for steel. Again, the bi-modal trend is more appropriate than Eqn. (1) in representing the data.

Figure 14 here

Figure 15 here

Figure 16 here

3. Discussion

The above plots are for data sets from a wide variety of independent sources, collected in separate test programs, at quite different times, in different geographic locations and by many different investigators. Irrespective of whether corrosion is measured as mass loss, pit depth or loss of tensile strength, the data sets from all these sources show that corrosion as a function of time predominantly has a bi-modal trend, similar in character (but not magnitude or timing) to that observed earlier for the corrosion of steel (Fig. 1). The examples also show that the power-law function Eqn. (1) almost always is not an adequate representation of corrosion trend, except perhaps (i) for quite short exposure durations falling in the period $0 < t < t_a$ in Fig. 1, or (ii) as a gross overall approximation that ignores the actual behaviour. Further, the various data sets and trends for atmospheric corrosion do not support a (approximately) linear function as was proposed earlier for corrosion loss over 10 years of exposure, or the monotonic semi-log function Eqn. (2) for maximum pit depth [10].

The pervasiveness of the bi-modal trend demands explanation. This is considered below but first a brief recapitulation of observations about the corrosion of aluminium in wet environments may be

helpful. As is well-known, immediately after first exposure to air aluminium very quickly develops a thin, compact and highly corrosion resistant oxide (passive) film consisting, at ambient temperatures, of γ -alumina [19]

This quickly hydrolyzes, in the presence of water or moisture, first to a thin (2-3nm) layer of boehmite [γ -AlOOH]

and then to bayerite [$\text{Al}(\text{OH})_3$ or $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$]

Typically the [bayerite](#) layers are around 20-40 microns thick but can reach more than 70 microns in industrial atmospheres [19]. The phase changes represented by reactions (4) and (5) show that even after relatively short-term exposures there can be a complex mix of corrosion products. In the presence also of chlorides the corrosion products may include AlCl_3 , $\text{Al}(\text{OH})\text{Cl}_2$ and $\text{Al}(\text{OH})_2\text{Cl}$ [4,31], all identified in practice [19,20]. They are associated with highly acidic solutions (pH in the range 1-3). This is consistent with aluminium corrosion being primarily associated with pitting [4].

As a result of increased corrosion through pitting, two interrelated scenarios are likely to develop: the topography of the corroding surface becomes, at the micro-level, increasingly more non-uniform and more non-homogenous and, as a result, the built-up thickness and properties of corrosion product also become increasingly more non-uniform and non-homogenous. This description is consistent with observations [19,32]. As a result there will be localization of environmental conditions on the corroding surface and of diffusion and similar characteristics of the corrosion product layer(s). It is also likely to produce local regions with very low oxygen concentration levels or in extreme cases anoxic conditions. The net effect is that differential aeration cells are likely to be established over the corroding surface superficially, at least, randomly distributed. In turn this establishes conditions sufficient for the initiation and progression of crevice and pitting corrosion under anoxic conditions, with cathodic oxygen reduction occurring in the shallower regions where oxygen diffusion is sufficient to sustain the rate of the reaction [4,

23,24,32]. The scenario up to this point in the progression of corrosion may be considered to correspond to phases 0-2 of the bi-modal model, i.e. for $t < t_a$ (Fig. 1).

The further development of corrosion product on the surface and particularly over the pits will lead to more anoxic locations within pits and the development of the scenario proposed by Wranglen [23] for the pitting of aluminium (see also Shreir [24] who noted the similarity to the mechanism of pitting corrosion of steel). Under these anoxic conditions the most likely reactions are the dissociation of water $\text{H}_2\text{O} \rightarrow \text{OH}^- + \text{H}^+$ and the concurrent cathodic hydrogen ion reduction reaction $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ (gaseous). Together these become $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^- + \text{H}_2$ (gaseous) and with the (anodic) aluminium oxidation reaction $\text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}^-$ the overall oxidation reaction may be written as:

As for Eqn. (3) to (5) the corrosion product Al_2O_3 hydrolyses to $\text{Al}(\text{OH})_3$ provided sufficient water is available and the pH is sufficiently low. This is the usual case for corrosion within pits [4,33]. Moreover, under these conditions pitting usually is considered an autocatalytic process as a result of the hydrogen ions generated by Eqn. (6) lowering the pH within the pits [4,23,24,34]. The rate and depth of pitting is controlled by the potential drop through the depth of the pit and may be influenced by the presence of chloride (or other aggressive) ions [35,36]. The overall description given here may be considered to correspond to the early part of phase 3 (Fig. 1), i.e. for $t > t_a$.

Since reactions (3-5) and (6) have similar corrosion products, it is not possible to determine from the corrosion products alone whether and to what extent reaction (6) occurs as part of the second mode of the bi-modal model, that is for $t > t_a$ (Fig. 1). However, there is other evidence that supports the autocatalytic nature of reaction (6) in the later part (i.e. for $t > t_a$) of the pitting process for aluminium. These include (i) the observation of hydrogen bubbles emanating from corrosion pits, including the deduction that this is caused by the hydrogen evolution reaction [4,23,24,37], (ii) that localized pitting after 20 years atmospheric exposure can be relatively deep compared to the rest of the surface corrosion [32] and (iii) that pit depth increases substantially for $t > t_a$ as shown, for example, in Figs. 8 and 9.

Further support for the transition from oxygen reduction to hydrogen ion reduction as the primary cathodic reaction through the time period around t_a is as follows. Firstly, oxygen reduction (in the first mode of the bi-modal model) is likely to be rate-controlled by oxygen transport through the corrosion products towards the corroding surface and hydrogen ion reduction (in the second mode)

by the rate of gaseous hydrogen transport away from the corroding surface, again through the corrosion product layer. In the case of aluminium, the corrosion product layer is likely to be thin. It follows that the rate of transfer of species - inward for oxygen and outward for hydrogen – most likely is controlled by effusion rather than diffusion [38]. Since rates of effusion are inversely proportional to the square root of the molecular weight of the species, in theory hydrogen gas should effuse four times faster than oxygen for the same effusion barrier. This means that the instantaneous rate of corrosion r_b leading up to t_a and the rate r_a sometime after t_a (Fig. 1) should be in the ratio 1:4. In practice not all points on the corrosion interface or at all pits will changeover at precisely the same time (the theoretical time t_a) and thus some transition period is to be expected, as indeed can be seen in (almost) all cases in Figs. 2-15. The changeover of local rates of corrosion will depend also on local conditions but on average these are likely to be similar for both r_b and r_a . Because the trend lines for some of the plots in Figs. 2-15 were made subjectively, accurate assessment of r_b and r_a and hence the ratio r_a / r_b is not possible, but it is clear from visual inspection of the plots that in most cases the ratio is around 4. Accurate determination either of the change in slope of the corrosion loss curves, or of the rates of oxygen consumption and hydrogen evolution is required for more detailed investigation.

Hydrogen gas effusion cannot continue to remain as the rate limiting step for very long. Most likely other aspects involved in reaction (6) will take over. These may include the build-up of corrosion product near the mouth of each pit, the inward diffusion of water through the corrosion product layer, the outward diffusion of aluminium ions or, much less likely, the kinetics of the reactions. The effect will be polarization of reaction (6) and the corresponding decreasing instantaneous corrosion rate, as seen for many of the trends in Figs. 2-15 and as shown schematically by the later part of phase 3 and by phase 4 in Fig. 1. It is considered that the most likely rate limiting step will be the outward diffusion of metallic ions through the corrosion product layer [39] but again this remains a matter for further investigation.

The proposed change over from oxygen reduction (in the first mode, Fig. 1) to hydrogen ion reduction (in the early part of the second mode) depends, as noted, on the development of anoxic conditions that permit, eventually, autocatalytic pitting. This will be a gradual process, as also evident from the change from the first to the second mode in Fig. 1. However, the timing of the transition modelled, in the limit, by t_a is not an immediately obvious consequence. Most likely this will need to be investigated by detailed modelling of the reactions and processes involved in the transition, perhaps following the pattern used earlier for modelling pitting processes [36,36]. The estimation and quantification of t_a and the other parameters describing the bi-modal model (Fig. 1) is a matter of considerable practical interest but is likely to pose a significant challenge. At a

simpler, more empirical, level the theoretical discussion given above should provide a sufficient basis for developing the mathematics for the parts of the model of Fig. 1 governed by diffusion processes, and for calibrating the model to in-situ data, similar to what has been done for steel [15].

Some aspects of the bi-modal model relate directly to practical observations. For example, it is well-known that deaerated waters are harmful to aluminium, producing rapid rates of pitting [2]. Corrosion in such waters would by-pass all the reactions that involve oxygen as the electron acceptor and only reaction (6) would occur and it is likely to be limited by criteria other than effusion through a corrosion product layer since a significant layer is unlikely to be formed under deaerated conditions. Reaction kinetics may then be rate limiting but since these are very much faster than any effusion process the corrosion rates will be very fast, initially at least, until corrosion products build-up to then begin to control effusion rates. This may account for the known early aggressive nature of aluminium corrosion under deaerated conditions.

Atmospheric exposure conditions may involve the deposition of sulfur dioxide and other species on the metal surface. Such deposition will invoke reactions additional to those described above and in consequence may affect the instantaneous rate of corrosion $r(t)$ at any time t . This includes the initial corrosion rate $r(t) = r_0$ at $t = 0$. Such exposure conditions also may affect the characteristics of the corrosion products and thus influence the rate of diffusion of species through them, particularly some time after initial exposure. The magnitudes of the corrosion rates r_b and r_a (Fig. 1) are likely to be affected (but not their ratio r_b / r_a as this is considered to be determined by relative effusion rates through a similar corrosion product layer around time t_a - see above). The effect on the rate r_a relative, say, to the initial corrosion rate r_0 could explain why in industrial and urban atmospheres r_a tends to be relatively high while in rural and some coastal atmospheres r_b tends to be relatively low. It is a matter with potential for further investigation.

Also of practical interest is whether aluminium is prone to microbiologically influenced corrosion (MIC). Conventionally, this is discounted as a significant influence except for algal involvement in the pitting corrosion of aluminium aircraft fuel tanks [3]. In early studies the obligatory anaerobic sulfate reducing bacteria (SRB) were implicated [40] but the presence of *Pseudomonas aeruginosa* also was noted. This species, nominally aerobic, produces metabolic products similar to those of SRB. Another laboratory study, using salt water (rather than seawater) to which cultures of SRB had been added found severe pitting after 12 months exposure [41]. The SRB were implicated as the cause. However, in a much shorter study of only 7 days in natural flowing seawater doubt was

expressed as to whether the very sparsely distributed areas of pitting were the result of microfouling (and hence differential aeration effects) or of MIC [42]. From a different perspective, it is known that under normal conditions aluminium and its alloys themselves are not toxic to microorganisms. Only its ionic forms, such as occur under low pH conditions, are toxic [43,44]. This suggests that MIC is unlikely to occur on the surface of aluminium although microfouling and thus differential aeration might. Further, MIC is unlikely to contribute to corrosion within and immediately adjacent to pits and near pit mouths since the low internal pit pH would provide ionic aluminium that is toxic to microorganisms. This also is a topic for further investigation.

Finally it is of interest why, apart from the observation reported by Morcillo et al. [18], the bi-modal behaviour has not been highlighted in previous studies of the long-term corrosion of aluminium. This contrasts, incidentally, with atmospheric (and seawater) corrosion of steels for which inconsistency with the power-law (Eqn. 1) had been noted already in 1992-3 [45,46,47] and for which the bi-modal model has been proposed subsequently as more appropriate [21,48]. One reason could be preconceptions of what is expected, based on what has been done before. For example, Sowinski and Sprowls [9] reported extensive data sets for 30 years of exposure. They gave what they termed 'eye-balled' (i.e. subjective) trends (Fig. 17) that certainly are not consistent with the power law $c(t) = At^B$. However, they discarded these in favour of the power law because, as they note, that was the expectation for the corrosion loss function.

Figure 17 here

Similarly, there are references in the literature to some data points, not consistent with the power law, being dismissed as caused by (unexplained) experimental error or by natural variability or as being outliers that are in some unspecified way claimed to be inconsistent with the rest of the data. The apparently long history of successful application of the power law to many different data sets tends to reinforce the view that it is appropriate, particularly when it is sometimes claimed as being a 'natural law' [49]. It can now be seen to be limited in its range of applicability as was noted previously in relation to the marine corrosion of steel [11,13,14,15]. The third reason is perhaps more insidious. It is that many experiments are planned with the power law as the basis for decisions about when to make observations. The power law usually is taken to imply that increasingly longer time intervals between observations are justified. However, such an experimental schema may cause crucial changes in trend to be missed.

5. Conclusion

Almost all empirical data for long-term corrosion of aluminium shows corrosion loss trends that are not consistent with the power-law model. Instead, the data show a much greater affinity for the bi-modal function. This is the case for the corrosion of aluminium alloys in fresh waters, seawaters and in various atmospheric exposure conditions and is supported by the experimental data provided by many different investigators in multiple longer-term exposure programs.

It is proposed that the bi-modal function is the result of the build-up of corrosion products causing a change in the corrosion process from being initially governed by oxygen reduction to later being governed by hydrogen ion reduction, in each case controlled by effusion considerations. Further build-up of corrosion products forces polarization of this mechanism in the longer term, most likely governed by the outward diffusion of aluminium ions through the corrosion products, principally those over the pits.

The present results have implications for the design of long-term corrosion experiments since using the conventional power law to plan data collection intervals may cause crucial changes in corrosion behaviour to be missed.

Acknowledgement

The financial support of the Australian Research Council is gratefully acknowledged.

References

- [1] M. Schumacher (Ed.), *Seawater Corrosion Handbook*, New Jersey, Noyes Data Corp., 1979.
- [2] G. Kreysa, R. Eckermann, *Dechema Corrosion Handbook*, Vol. 11, New York, VCH Publishers, 1992.
- [3] C. Vargel, *Corrosion of Aluminium*, London: Elsevier, 2004.
- [4] Z. Szklarska-Smialowska, Pitting corrosion of aluminum, *Corros. Sci.* 41 (1999) 1743-1767.
- [5] C.J. Walton, D.O. Sprowls, J.A. Nock, Resistance of aluminum alloys to weathering, *Corrosion*, 9 (1953) 345-358.
- [6] C.R. Southwell, A.L. Alexander, C.W. Hummer, Corrosion of metals in tropical environments - Aluminum and magnesium, *Mat. Prot.*, 4(12) (1965) 30-35.
- [7] W.H. Ailor, Performance of aluminum alloys at other test sites, (In) *Metal Corrosion in the Atmosphere*, ASTM Special Technical Publication No 435, Philadelphia, American Society for Testing and Materials, 1968, 285-307.

- [8] E. Mattsson, S. Lindgren, Hard-rolled aluminum alloys, (In) Metal Corrosion in the Atmosphere, ASTM Special Technical Publication No 435, Philadelphia, American Society for Testing and Materials, 1968, 240-256.
- [9] G. Sowinski, D.O. Sprowls, Weathering of aluminum alloys, W.H. Ailor (Ed), Atmospheric Corrosion, New York, John Wiley, 1982, 297-328.
- [10] E. Otero, R. Lizarbe, S. Feliu, Behaviour of aluminium during 10 year's exposure at a coastal test site at Alicante, British Corros. J. 13(2) (1978) 82-84.
- [11] G. Tammann, Lehrbuch der Metallographie, 2nd Edn., Leipzig, Leopold Voss (1923).
- [12] M. Pourbaix, The linear bilogarithmic law for atmospheric corrosion, W.H. Ailor (Ed), Atmospheric Corrosion, New York, John Wiley, 1982, 107-122.
- [13] F. Booth, A note on the theory of surface diffusion reactions, Trans. Faraday Soc., 44 (1948) 796-801.
- [14] U.R. Evans, The corrosion and oxidation of metals: scientific principles and practical applications, London, Edward Arnold, 1960.
- [15] R.E. Melchers, Mathematical modelling of the diffusion controlled phase in marine immersion corrosion of mild steel, Corros. Sci., 45(5) (2003) 923-940.
- [16] P.M. Aziz, H.P. Godard, Pitting characteristics of aluminum – Influence of magnesium and manganese, Journal of Industrial and Engineering Chemistry, 44(8) (1952) 1791-1795.
- [17] H.P. Godard, The corrosion behavior of aluminum in natural waters. Can. J. Chem. Eng., 38 (1960) 167- 173.
- [18] M. Morcillo, J. Simancas, S. Feliu, Long-term atmospheric corrosion in Spain: Results after 13-16 years of exposure and comparison with world-wide data, W.W. Kirk, H.H. Lawson (Eds.), Atmospheric Corrosion, ASTM STP 1239, Philadelphia, American Society for Testing and Materials, 1995, 195-214.
- [19] D. de la Fuente, E. Otero-Huerta and M. Morcillo, Studies of long-term weathering of aluminium in the atmosphere, Corros. Sci., 49 (2007) 3134-3148.
- [20] S. Sun, Q. Zheng, D. Li, J. Wen, Long-term atmospheric corrosion behaviour of aluminium alloys 2024 and 7075 in urban, coastal and industrial environments, Corros. Sci., 51 (2009) 719-727.
- [21] R.E. Melchers, Modeling of marine immersion corrosion for mild and low alloy steels - Part 1: Phenomenological model, Corrosion, 59 (4) (2003) 319-334.
- [22] R.E. Melchers, R. Jeffrey, The critical involvement of anaerobic bacterial activity in modelling the corrosion behaviour of mild steel in marine environments, Electrochim. Acta, 54 (2008) 80-85.
- [23] G. Wranglen, Introduction to corrosion and protection of metals, Butler and Tanner, London, 1972.

- [24] L.L. Shreir, Localised corrosion, L.L. [Shreir](#), R.A. Jarman, G.T. Burstein (Eds.), Corrosion, Vol. 1, (3rd Edn.), Oxford, Butterworth-Heinemann, 1994, 1-151-1:212.
- [25] R.W. Stineman, A consistently well-behaved method of interpolation. Creative Computing, July 1980.
- [26] C.J. Walton, W. King, Resistance of aluminium base alloys to twenty-year atmospheric exposure, Symposium on Atmospheric Corrosion of Non-ferrous Metals, ASTM-STP 175, Pennsylvania, American Society for Testing and Materials, 1955, 21-44.
- [27] M. Natesan, G. Vankatcchari, N. Palaniswamy, Kinetics of atmospheric corrosion of mild steel, zinc, galvanized iron and aluminium at 10 exposure stations in India, Corros. Sci. 48 (2006) 3584-3608.
- [28] J.R. Vilche, F.E. Varela, G. Acuna, E.N. Codaro, B.M. Rosales, A. Fernandez, G. Moriena, A survey of Argentinean atmospheric corrosion: I – Aluminium and zinc samples, Corros. Sci. 37(6) (1995) 941-961.
- [29] Y.N. Mikhailovzki, P.V. Strekalov, Atmospheric corrosion testing in the USSR, W.H. Ailor (Ed), Atmospheric Corrosion, New York, Wiley-Interscience, 1982, 923-942.
- [30] J. M. Chambers, W. S. Cleveland, B. Kleiner, P.A. Tukey, Graphical Methods for Data Analysis, Boston, Duxbury Press, 1983.
- [31] R.T. Foley, N. Nguyan, The chemical nature of aluminum corrosion, J. Electrochem. Soc., 126(3) (1982) 464-467.
- [32] M. Lashermes, A. Guilhaudis, M. Reboul, G. Trentelives, Thirty-year atmospheric corrosion of aluminium plates in France, M.H. Ailor (Ed.), Atmospheric Corrosion, 1982, 353-364.
- [33] Z. Szklarska-Smialowska, Pitting Corrosion of Metals, Houston, NACE, 1986.
- [34] G. Wranglen, Pitting and sulphide inclusions in steel, Corros. Sci. 14 (1974) 331-349.
- [35] A. Turnbull, Mathematical modelling of localized corrosion, K.R. Trethewey and P.R. Roberge (Eds.), Modelling Aqueous Corrosion: From Individual Pits to System management, NATO ASI series E, Vol. 266, Dordrecht, Kluwer Academic Publishers, 1994, 79-63.
- [36] E. McCafferty, Sequence of steps in the pitting of aluminium by chloride ions, Corros. Sci. 45 (2003) 1421-1438.
- [37] C.B. Barger, R.C. Benson, Analysis of the gases evolved during the pitting corrosion of aluminum in various electrolytes, J. Electrochem. Soc. 127 (1980) (11) 2528-1530.
- [38] T.L. Brown, H.E. Lemay, Chemistry: The central science (2nd Ed), Englewood Cliffs, NJ, Prentice-Hall, 1981.
- [39] G.T. Burstein, C. Liu, R.M. Souto, S.P. Vines, Origins of pitting corrosion, Corros. Engrg. Sci. Techn. 39 (1) (2004) 25-30.

- [40] H.G. Hedrick, C.E. Miller, J.E. Halkias, J.E. Hildebrand, Selection of a microbiological corrosion system for studying effects on structural aluminium alloys, *Appl. Microbiol.*, 12 (1964) (3) 197-200.
- [41] A.K. Tiller and G.H. Booth, Anaerobic corrosion of aluminium by sulphate-reducing bacteria, *Corros. Sci.* 8 (1968) 549-555.
- [42] H.A. Videla, M.F.L. de Mele and G. Brankevich, Assessment of corrosion and microfouling of several metals in polluted seawater, *Corros. Sci.* 44 (1988) (7) 423-426.
- [43] D.J. Spry, J.G. Weiner, Metal bioavailability and toxicity to fish in low-alkalinity lakes: A critical review, *Env. Poll.*, 71(1991) (2/4) 243-304.
- [44] J.E. Amonette, C.K. Russell, K.A. Carosino, N.L. Robinson, J.T. Ho, Toxicity of Al to *Desulfovibrio desulfuricans*, *Appl. Environ. Microbiol.*, 69 (7) (2003) 4057-4066.
- [45] R.H. McCuen, P. Albrecht, J. Cheng, A new approach to power-model regression of corrosion penetration data, V. Chaker (Ed.) *Corrosion Forms and Control for Infrastructure*, Special Technical Publication STP 1137, American Society for Testing and Materials, West Conshohocken, PA, 1992.
- [46] M. Morcillo, S. Feliu, J. Simancas, Deviation from bilogarithmic law for atmospheric corrosion of steel, *Brit. Corros. J.* 28 (1) (1993) 50-52.
- [47] J.H. Wang, F.I. Wei, Y.S. Chang, H.C. Shih, The corrosion mechanisms of carbon steel and weathering steel in SO₂ polluted atmospheres, *Mater. Chem. Phys.* 47 (1) (1997) 1-8.
- [48] R.E. Melchers, A new interpretation of the corrosion loss processes for weathering steels in marine atmospheres, *Corros. Sci.* 50 (2008) 3446-3454.
- [49] R. Vera, B.M. Rosales, C. Tapia, Effect of the exposure angle in the corrosion rate of plain carbon steel in a marine environment, *Corros. Sci.* 45 (2003) 321-337.

Bi-modal trend in the long-term corrosion of aluminium alloys

FIGURES

Figure 1. Schematic bi-modal model for long-term corrosion loss and pit depth in marine environments. In the idealized case the change from predominantly oxidic to predominantly anoxic conditions occurs at t_a with a change of instantaneous corrosion rate from r_b to r_a .

Figure 2. Data and interpreted trends for Al 1100 exposed to marine immersion and tidal immersion conditions. Data from Southwell, et al. [6].

Figure 3. Data and interpreted trends for Al 6061T exposed to marine immersion and tidal immersion conditions. Data from Southwell, et al. [6].

Figure 4. Data and interpreted trends for Al 1100 and Al 6061T exposed to freshwater immersion conditions (Gutan Lake, PCZ). Data from Southwell, et al. [6].

Figure 5. Loss of tensile strength data for several grades of aluminium under coastal marine atmospheric exposure conditions at La Jolla, California, together with interpreted data trends. Data from Walton and King [26].

Figure 6. Data and trends (interpreted where shown) for unspecified aluminium exposed to marine atmospheric conditions at several sites in India. Data from Natesan et al. [27].

Figure 7. Data and trends (interpreted where shown) for unspecified aluminium exposed to industrial atmospheric conditions at two sites in India. Data from Natesan et al. [27].

Figure 8. Data and best fit trends (one with a slight interpretation) for maximum pit depth on aluminium alloys exposed to industrial atmospheric conditions in Sweden. Data from Mattson and Lindgren [8].

Figure 9. Data and best fit trends for maximum pit depth on aluminium alloys exposed to urban marine atmospheres in Sweden. Data from Mattson and Lindgren [8].

Figure 10. Data and best fit trends as obtained from a plotting routine, for aluminium alloys exposed to coastal marine atmospheres in Argentina, showing two alternative interpretations for apparent inconsistent data and trends at Jubany. Data from Vilche et al. [28].

Figure 11. Data and piece-wise linear trends for 99.5% pure aluminium exposed to industrial-urban and marine-urban atmospheres in Russia. Data from Mikhailovski and Strekalov [29].

Figure 12. Data and trends (interpreted where shown) for Al 2024 for industrial, marine coastal and urban exposures. Data from Sun et al. [20].

Figure 13. Data and trends, without interpretation for Al 7075 for industrial, marine coastal and urban exposures. Data from Sun et al. [20].

Figure 14. Data and trends, without interpretation, as obtained directly from the best-fit plotting routine, for 99% pure aluminium exposed to severe marine, mild marine and industrial atmospheres in Spain. Data from de la Fuente et al. [19].

Figure 15. Data and trends, without interpretation, obtained directly from the best-fit plotting routine, for 99% pure aluminium in rural and urban atmospheres in Spain. Data from de la Fuente et al. [19].

Figure 16. The same data as in Figure 15 plotted on a log-log plot and showing two different trends for each data set, consistent with the bi-model model.

Figure 17. Data for loss of tensile strength for 3 aluminium alloys showing so-called eye-balled trends (bold) and the power-law (light) fitted to the same data.