Original article

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Nonlinear trending of corrosion of high nickel alloys in extended marine and atmospheric exposures

<https://doi.org/10.1515/corrrev-2020-0079>

Received August 16, 2020; accepted October 7, 2020;

published online October 28, 2020

Abstract: The relatively limited data for the corrosion and pitting of high nickel alloys are reviewed herein and time-dependent trends developed for exposures in marine and atmospheric environments. Data sets for average or ‘uniform’ corrosion losses that are sufficiently extensive show topological consistency with the bimodal functional model previously observed for steels and various copper-nickel and aluminum alloys. Trends for localized corrosion (pit or crevice depth) plateau after earlier rapid growth over several years. The present observations add support to the concept that there is a change in corrosion behavior with extended temporal exposure and that this is generally consistent for many alloys. They also reinforce that shorter-term observations of maximum corrosion or pit depth usually is unsuited for extrapolation to, and prediction of, longer-term corrosion as typically important for practical infrastructure applications.

Keywords: atmospheric; corrosion; immersion; modelling; nickel; pitting.

1 Introduction

This paper is concerned with the development of corrosion of high nickel (Ni) alloys exposed in marine and atmospheric environments over extended periods of time (years, decades). This is a precursor to the development realistic physico-chemical-mathematical models as distinct from purely empirical models, relevant for high-quality prediction of likely future expected corrosion of infrastructure (Melchers 2003a, 2018). The present paper focuses on

commercial high nickel alloys and their general corrosion, as measured by coupon mass loss, and depth of localized corrosion such as pitting and crevice corrosion.

Extensive empirical experience has shown that commercial high Ni alloys can be very resistant to corrosion in severe operating and environmental conditions (Davis 1998), particularly under high water velocities (LaQue 1941). Their high resistance to general corrosion in atmospheric, freshwater and seawater exposures is attributed to the development and maintenance of a high resistant passive nickel-oxide film. Both electrochemical testing and short-term field exposures (e.g. 1–2 years) has shown that the average short-term corrosion rates are very low (typically < 2.5 $\mu\text{m}/\text{year}$) (Crum 1995; Friend 1980). However, short term tests also show that under deposits and under fouling, particularly in stagnant or near-stagnant immersion exposures (e.g. at rates up to 0.5 m/s), they may suffer significant localized corrosion (pitting, crevice) (Combrade 2012; Klapper et al. 2017; Niederberger et al. 1970; Uhlig, 1948). Whether such short-term results carry over to the longer-term corrosion of interest for infrastructure applications is an important practical issue, explored further herein.

The next section gives a brief review of nickel alloys. This is followed by a review and interpretation of data sets that are available for longer-term exposures in marine and in atmospheric conditions. From these data sets trending patterns for mass loss and for maximum localized corrosion such as depth of pitting or crevice corrosion are considered, using as a guide the bimodal model previously shown as relevant for steels, cast irons and for a variety of copper and aluminium alloys. The corrosion mechanisms likely involved are discussed and the possibility for involvement of microbiologically influenced corrosion (MIC) considered. Comments are made about the practical implications and potential areas for further research.

2 Background

Much of the world's production of nickel is used for stainless steels. However, a wide variety of specialist high

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nickel alloys are available for specific applications. They can be divided into three broad groups—those that are almost pure Ni or with very high Ni content, those alloyed primarily with copper, and those alloyed mainly with chromium (Table 1). Their corrosion resistance depends much on the corrosion product that is generated during early exposures. For example, Nickel 200 (N02200), a commercial pure nickel, may develop a grey patina in industrial atmospheres as a result of a thin adherent rust film, mostly containing sulfur oxides.

Nickel alloys tend to be used for very specific applications. For example, alloys N06625, N04400 and N05500 have been specified for US naval vessels for areas in contact with seawater (Davis 1998) such as for heat-exchanger tubes (Nicklin 2008). Nickel alloys, even with Cr, are prone to pitting and crevice corrosion, particularly under deposits or under fouling likely to form in stagnant and low velocity waters (LaQue 1969). This is more so in seawater (Little et al. 1990; Maylor 1978). Typically pitting occurs soon after first exposure, proceeds relatively rapidly for some 2–3 years and then slows considerably. The maximum depth of localized corrosion or pitting in that time period depends very much on alloy composition, being around 1.4 mm for the Ni–Cu alloy N04400, about 0.025 mm for the Ni–Cr–high Fe alloy N08250 and very little for the high Ni–Cr–low Fe alloy N06625 (Table 1) (Davis 1998).

Particularly for infrastructure applications the manner in which localized corrosion such as pitting and corrosion loss develops with continued exposure is important in

understanding how short-term observations might relate to longer-term corrosion, noting that for most alloys the relationship is not a simple one. For a number of different alloys, including mild and low alloy steels, cast iron, copper alloys and aluminium alloys, the so-called bimodal model (Figure 1) has been found to provide a good description of such development (Melchers 2018). This suggests the bimodal characteristic is generic rather than alloy-type specific.

A particular feature of the bimodal model is that with sufficient build-up of rusts, the corrosion process transitions from being under aerobic conditions, and therefore under the cathodic oxygen reduction reaction, to anaerobic conditions dominated by the hydrogen evolution cathodic reaction. The latter is considered to govern the development of longer-term corrosion, at least while the rusts remain in place to retain anaerobic conditions at the metal–corrosion–corrosion product interface. In atmospheric exposures it has been observed, for steels at least, that under advanced corrosion conditions some of the outer layer corrosion products may become oxidized, particularly under atmospheric conditions, and potentially exfoliate and be lost, or be removed through mechanical damage or lost through excessive mass compared with the strength of the rust layers. This is consistent with the theoretical mechanism for atmospheric rust layer development originally proposed by Evans and Taylor (1972) and, broadly, supported by experimental data (Stratmann et al. 1983). It is consistent also with empirical evidence that longer-term corrosion loss tends to be close to a linear

Table 1: Broad summary of compositions of the main high nickel alloys (based on Asadi and Melchers 2018).

Alloy (common name)	UNS no.	Ni (%)	Cu (%)	Other (%)
<i>Pure and high Ni alloys</i>				
Nickel 200 ^a	N02200	>99.0	<0.25	<0.75Fe, <0.25C
Nickel 201–290	N02201–N02290	>93.0–99.0	<0.25	<0.75Fe, <0.25C
Nickel 301	N03301	>93.0	<0.25	<0.75Fe, <0.25C
<i>Ni–Cu alloys</i>				
Alloy 400 (Monel), 405, 500	N04400, N04405, N04500	>63	28–34	<3
Alloy 401, 404	N04041, N04404	40–45, 52–57	bal.	3–4
<i>Ni–Cr–Fe alloys</i>				
Alloy 600	N06600	>72	14–17	Fe 6–10
Alloy 601–690	N06601–N06690	44–64	20–27	Fe 3–11
Alloy 7xx	N077xx	50–60	17–23	Nb 3–6, Fe bal.
<i>Fe–Ni–Cr–Mo alloys</i>				
Alloy 800	N08800	30–35	19–23	Mo 1, Fe 40
Alloy 825, 925	N08250, N09925	38–46	20–24	Mo 1, Fe > 22
<i>Ni–Cr–Mo–Fe alloys</i>				
Alloy B, B-2, B-3	N10001, N10665, N10675	42–65	1–3	Mo 26–32, Fe 1–7
Alloy C, C-276	N10002, N10276	60–65	15–17	Mo 15–17, Fe 4–7

^aCommercially pure nickel. Note: Trade names not included.

Figure 1: Schematic view of the bi-modal model for representing the development of corrosion loss as a function of time and the associated increasing build-up of corrosion products. The two modes are shown, as are the phases within the modes. In summary the dominant processes in each phase are: (0) establishment of chemical equilibrium between water and metal and invasion of metal surfaces by any species in the water, (1) short period of initial corrosion kinetic chemical reaction(s) limited by oxygen concentration diffusion from the water adjacent to the metal surface, (2) corrosion process increasingly rate limited by oxygen diffusion through increasing layers of corrosion products, (3) change to hydrogen diffusion being the corrosion rate limiting step, and reduction by further build-up of corrosion products, and (4) long-term semi-equilibrium between corrosion under rust layers and oxidation processes on the exterior rust surfaces, possibly with influence of microbiological activity.

function in time (Schumacher 1979), irrespective of the metal or alloy exposed.

Without venturing into the underlying corrosion mechanisms, herein it is hypothesized that overall the mechanisms in the bimodal model also apply to nickel alloys. In particular it may be expected that overall these alloys will have similar characteristics in corrosion loss development with time and also for corrosion product development, except exfoliation under atmospheric conditions, since that appears not to have been reported. This could be the result of the corrosion products for nickel alloys tending to be moderate in volume and of reasonable strength (Davis 1998). Based on the earlier exposition of the bimodal model, a ‘top-down’ view is that it consists primarily of two modes—an early, largely aerobic corrosion mode, followed by the second and indefinite-in-time mode during which anaerobic corrosion processes predominate. The phases (Figure 1) within those modes represent different dominant corrosion processes (Melchers 2003). As for steels (Melchers 2014), the second mode, under anaerobic conditions, is likely the main vehicle for the possibility, including for nickel alloys, of microbiological influenced corrosion, usually associated with anaerobic conditions (Little and Lee 2007). The time period $0-t_a$ where t_a nominally separates modes 1 and 2 reduces with

the dissolved oxygen (DO) content in the water or available at the corrosion interface (Melchers and Chernov 2010). This means that for reduced DO conditions mode two commences earlier and the amount of corrosion c_a at the end of mode one becomes less.

In the following the question of interest is whether the (mainly) field data available for the medium to longer term corrosion of nickel alloys can be interpreted as closely or even broadly consistent with the bi-modal trend (Figure 1), irrespective of any detailed calibration of the model to the data. To make this type of interpretation implies that a degree of judgement is necessary about topological similarities. It also requires recognition that all attempts at fitting a model to data or vice versa must involve some allowance for scatter and statistical uncertainty in the data. As will become evident, the corrosion data currently available for the degree of corrosion of nickel alloys at any point in time are insufficient to make other than very crude estimates of statistical uncertainty or scatter (such as might be measured by standard deviation). However it is reasonable to expect that in some respects scatter in corrosion data for nickel alloys is likely to be generally similar to scatter in data for other metal alloys. For example, for steel in seawaters especially designed studies showed coefficients of variation of around 0.05 in corrosion loss (Melchers 2003b).

3 Data sources

Atmospheric corrosion of nickels has been of interest since at least the 1920s. Most reported observations are for exposures of one year or less (Leygraf et al. 2016). One of the earliest long-term studies, for atmospheric corrosion losses at 5, 10 and 15 years, considered coupons from a 36% nickel-iron alloy exposed at four different sites (Colombo, Sri Lanka, Auckland, NZ, Halifax, Nova Scotia and Plymouth, UK) (Friend 1940). A linear trend was assumed to best fit the data for each site, producing average corrosion rates less than $5 \mu\text{m}/\text{year}$. A parallel set of trials at the same sites but in tidal seawater produced average corrosion rates up to $8\times$ higher and up to $12\times$ higher for seawater immersion. Unfortunately, without data for exposures less than five years and with only two other exposures per site it is not possible to employ the data to examine consistency with a nonlinear corrosion loss trend, such as the bimodal trend. These data are, therefore, not considered further. Other data sets, such as the 20-year US atmospheric exposure program commenced in 1933 (ASTM 1946) with coupon recoveries at 1, 3, 6, 10 and 20 years also cannot be used, since for the first six years of the test program,

recovered coupons were simply weighed and then re-exposed (Copson 1956). Failing to remove the rust products under-estimates the differences in corrosion mass loss compared with the actual metal mass loss for the early part of the test program. This also renders comparisons with the subsequent mass losses problematic. Fortunately, in this test program some of the coupons at each recovery were machined to form tensile specimens. Since the presence or otherwise of corrosion products has negligible or no effect on tensile strength, it can be used as a surrogate for mass loss. Therefore the data has some value and are considered in the next section. Interestingly, the report noted that unexposed, laboratory-stored coupons showed very small changes (a few percent) in material properties over the same 20-year period. However, it is readily verified that the associated small corrections are negligible relative the overall mass losses and therefore may be ignored.

A more conventional exposure program was conducted over 20 years at the industrial atmospheric exposure site at Bayonne NJ, using 0.8 mm thick nickel coupons, exposed vertically (and some others inclined at 30° to the horizontal) with mass losses determined after exposure and cleaning in the usual way (Copson 1956). In the following, only the corrosion losses for the vertical specimens are considered. The other data have insufficient recoveries for discrimination of subtleties in trends. Similarly, a subsequent test program using similar coupons (van Rooyen and Copson 1968) at Kure Beach (NC), Newark (NJ), Port Reyes (CA) and State College (PA) had only three recoveries (2, 7 and 20 years), again insufficient to discern nonlinear corrosion loss trends. It also is not used herein.

Haynes and Baboian (1988) reported corrosion rates that had been derived from coupon mass losses observed for recoveries at 0.5, 1.5, 3.5, 7.5 and 15 years at several different atmospheric tests sites, including marine and inland locations. The program used 0.8 mm thick (likely commercially) pure nickel coupons. It also exposed coupons consisting of a mild steel substrate with 0.13 mm nickel or Monel cladding. For the present study, all the reported corrosion rates were converted to mass losses.

The US Panama Canal Zone 16-year-exposure program has provided much corrosion loss and pit depth data, including for several nickel alloys (Southwell and Alexander 1967). Exposure data are available for seawater immersion, seawater half-tide and freshwater immersion corrosion loss and pit depth development and for coastal and slightly inland corrosion losses and pit depths, over a total period of 16 years, with several periodic recoveries. These data sets are considered in detail in the next section.

The effect of water velocity on corrosion of nickel alloys in seawater immersion and tidal conditions, whilst

potentially important, has had little research attention and limited information is available. Some general guidance was extracted from observations after two years continuous exposure (Niederberger et al. 1970). These tests indicated that Cr in conjunction with Mo may be beneficial in reducing pit depth and depth of crevice corrosion, but that alloy composition alone was an insufficient indicator of propensity to pitting corrosion. Again, the lack of data for multiple exposure periods renders these data unsuited for the present work. Similarly, experimental observations dealing with initiation of crevice corrosion for high nickel alloys (Asphahani 1980; France 1972; Friend 1980; Lillard et al. 1994) do not supply sufficient information about long-term trends, and are not considered herein.

For deep-sea exposures, some observations for nickel alloys are available (Weisert 1957; Wheatfall 1967). The most extensive (Reinhart 1976) is for immersion corrosion in the Californian Pacific Ocean, 70–80 nautical miles off Port Hueneme at depths to 6000 ft. (≈ 2000 m) for 75 different metals including nickel based alloys. Most were exposed for up to one year, but some for up to three years. Also, some coupons were partly buried in the sediments but no significant differences between these and those in immersion conditions were reported. At depths below about 500 m, water temperatures were 2–3 °C, dissolved oxygen concentrations were low and general corrosion was low to negligible, including for the more highly alloyed coupons, although there was some pitting and crevice corrosion.

4 Data interpretations – mass loss

The data considered in this section has been drawn directly from the original sources, and is presented in the original units on the primary axes, with soft conversion to metric units shown on the auxiliary axis, as detailed below. Marine immersion corrosion loss (as determined from mass loss to give one-sided coupon corrosion loss) is considered first, together with corrosion in the tidal zone. Attention is then given to corrosion loss for deep seawater conditions, followed by corrosion in the atmosphere.

4.1 Immersion and tidal corrosion – Panama Canal zone

The most extensive data for the corrosion of nickel and several pre-1950s nickel alloys in seawater is that for tropical condition in the Panama Canal Zone (PCZ) region (Southwell and Alexander 1967). Protocols equivalent to currently

accepted procedures for corrosion coupon preparation, exposure, recovery and cleaning and measurement were applied. For continuous immersion exposure in seawater the corrosion losses calculated from coupon mass-loss are shown in Figure 2 as individual data points, at years 1, 2, 4, 8 and 16, for 99% pure nickel (UNS N02200), for Monel and for hot-rolled Monel (UNS N04400), and for 70:30 CuNi alloy (UNS C71500) (See Table 1 for composition details). Using these points the light best-fit lines were drawn using the Stineman (1980) computer-based algorithm. It is based on the use of rounded linear interpretation between points. This ensures continuity of both the function and the gradient. Note that the fitted curves pass through all relevant data points. Figure 2 also shows bold trend lines. These are considered, subjectively, to reflect more closely the bimodal trend expected according to Figure 1. They also pass through all the data points and are, in most cases, very similar to the light lines obtained using the Stineman function. Only in the case of 99% pure nickel are there some (relatively small) regions of differences between the lines, but not, of course, at the observation (data) points. As can be seen more clearly in Figure 2b, the trend in the data for the first two years shows a gradually declining instantaneous rate of corrosion, but then, between 2 and 4 years, the rate increases again and even more so between 4 and 8 years. This behavior is consistent with the bimodal model, and has been used to construct the interpreted trend shown. Overall, it is reasonable to conclude that all four alloys in Figure 2 exhibit bimodal trending.

A very similar situation can be seen for coupon corrosion loss in the mid-tide zone (Figure 3). The exposure sites were the same as those for the immersion test sites. For clarity, Figure 3b shows the first eight years in more detail.

As before, the light-colored trends were obtained using the Stineman computer-based algorithm and the bold lines are subjective fits to the data points. Also as before, only for the 99% nickel is there some divergence between the subjective trend and the smooth fit Stineman curve but not, of course, at the data points. In all cases in Figure 3b the subjective trends are not inconsistent with the data and with the expectations from the bimodal model.

4.2 Deep sea immersion corrosion – off California

The extensive data for corrosion of a wide variety of metals and alloys in the deep sea (1750 m), low dissolved oxygen (1.4 ml/l) environment of California includes some older nickel alloys (Reinhart 1976). Most are for periods of observation less than one year, but there are also some coupon sets with systematic observations at 0.34, 1.1, 2.06 and 2.92 years. Only the latter are considered here (Figures 4–6). The corrosion losses for alloys N02200 and N02201 in immersion and sediment exposures are shown in Figure 4. Also shown are the added light colored trends obtained using the Stineman best fit algorithm. Both immersion corrosion and corrosion in the local sediments (not defined in the source document) are shown. The interpreted trends, in bold, are shown also, passing where possible through the mean of all data points at any observation time point.

Similar plots are shown in Figures 5 and 6 for N02210 and N02211, and N03301 and N04406, respectively. Reinhart (1976) also reported other data sets for other nickel alloys, including some in the lower 400 series. These are

Figure 2: Corrosion loss data and trends for nickel–copper alloys under tropical immersion exposures for up to 16 years (a) 0–16 years, (b) expanded version for 0–8 years.

Figure 3: Corrosion loss data and trends for nickel–copper alloys under tropical mid-tide exposures for up to 16 years (a) 0–16 years, (b) expanded version for 0–8 years.

not shown here because they have considerable inconsistencies in the data, such as observations with much lower corrosion losses for longer exposures. Physically this is impossible for any given alloy, even allowing for some scatter or variance in the corrosion between nominally identical coupons. Figures 5a and 6a also show such inconsistencies, but in these cases it is possible to postulate two different (‘alternate’) interpretations of the data, as shown. Irrespective of which is the correct interpretation, the overall trends in each case exhibit bi-modal behaviour. The possible reasons for this type of inconsistency are considered in the Discussion. It also considers the delayed onset of mode two for the sediment exposure in Figure 5b.

4.3 Marine atmospheric corrosion—Panama Canal zone

Turning now to corrosion in the atmosphere, Figure 7 shows corrosion loss data for the coastal atmospheric exposure site and for the inland atmospheric exposure site, both in the PCZ (Southwell and Alexander 1967). The coastal site is on the coast at Miraflores, PCZ and the inland site is about 2.5 km inland from there. In each case Stineman smooth curves have been computer-fitted through the data sets. In Figure 7a the bimodal trends can be discerned without interpretation. Almost the same situation holds for the data and trends for the inland exposures

Figure 4: Corrosion loss data and trends over three years exposure in low dissolved oxygen deep sea conditions for (a) nickel alloy N02200 and (b) nickel alloy N02201, showing trends for immersion corrosion and for coupons in sediments. Details of the exposure in sediments are not provided in the original report (Reinhart 1976).

Figure 5: Corrosion loss data and trends over three years exposure in low dissolved oxygen deep sea conditions for (a) nickel alloy N02210 and (b) nickel alloy N02211, showing trends for immersion corrosion and for coupons in sediments. Details of the exposure in sediments are not provided in the original report (Reinhart 1976).

Figure 6: Corrosion loss data and trends over 3 years exposure in low dissolved oxygen deep sea conditions for (a) nickel alloy N03301 and (b) nickel alloy N04406, showing trends for immersion corrosion and for coupons in sediments. Details of the exposure in sediments are not provided in the original report (Reinhart 1976).

(Figure 7b). It is clear that the trends in the data points can be interpreted as shown with the bold lines, and also that these deviate only slightly from the Stineman algorithm computer-fitted trends (shown light).

4.4 US mainland atmospheric corrosion

Atmospheric corrosion mass loss data reported by Haynes and Baboian (1988) for several US mainland sites are shown in Figure 8. All coupons were commercial pure nickel and of the same size ($4 \times 6 \times 5/16$ in.) ($100 \times 150 \times 0.81$ mm) and therefore only the mass loss (in

grams) is shown. The amount of mass loss (corrosion loss) varies very considerably, with those shown in Figure 8a about $5 \times$ greater than those in Figure 8b. Note the quite different vertical scales between the two figures.

As before, the Stineman smooth curve function was fitted to the data as reported and shown in Figure 8 for each case. Also shown are the interpreted trends obtained in the same way as before, ensuring that they pass through the reported data and allowing for changes in trend that are evident in the data from one observation point to the next. It is seen that the relative severe marine corrosion test site at Kure Beach provides trends that are closely bimodal, but that this is less easy to discern for the mild marine site at

Figure 7: Corrosion loss data and trends for several nickel–copper alloys under tropical atmospheric conditions for up to 16 years (a) coastal exposure, (b) inland exposure.

Figure 8: Corrosion loss of commercial pure nickel as measured by mass loss for several different US mainland exposure sites.

Miami. Similarly, for the severe rural and industrial sites, bimodal trending is evident, even without much interpretation (such as for Anaheim).

The same authors reported corrosion losses for (mild) steel clad with 0.15 mm of Monel and exposed at several mainland USA locations. These have been separated into the more aggressive sites (Figure 9a) and the less aggressive sites (Figure 9b). In all cases, the Stineman trends through the data show trending that is very close to bimodal, or is easily interpreted as such. The mass loss at 14.5 years for Newark is likely limited by the thickness of the nickel cladding. In Figure 9b there are two data points that appear inconsistent, marked '?'. Again, the possible reasons for these are considered in the Discussion.

A different set of data is shown in Figure 10 for atmospheric corrosion at Bayonne (NJ), a site that is nominally industrial (Copson 1956). As before, the Stineman smooth fit curve is shown through the data together with the interpreted trend based on the notion of consistency with other trends for mass loss at industrial atmospheric test sites. The smooth fit curve (light line) interprets the data as corrosion accelerating with increasing exposure period. This is clearly inconsistent both with other empirical observations and with expectations for extended corrosion periods. A more plausible trend is the subjective trend, shown bold. It suggests that long-term corrosion trends close to linear.

Data for corrosion loss of commercially pure nickel exposed at two other industrial sites are shown in

Figure 9: Corrosion loss, as measured by mass loss, of commercial pure nickel cladding on a mild steel substrate for several different US mainland exposure sites.

Figure 11a, while Figure 11b shows results for Monel at the same sites as well as another.,

In all cases it is evident, either directly from the data trend or from the interpreted trends, that a bimodal functional form may be considered consistent with the reported data (Copson 1956).

In both cases the corrosion losses are shown in terms of reduction in tensile strength. This can be considered indicative of general corrosion loss—direct conversion

from strength to corrosion loss was found to be problematic owing to insufficient data being supplied in the original data source. Despite this, it is evident that in all cases the data trending is consistent with the bimodal functional form.

5 Depth of localized corrosion

There are many qualitative observations regarding the resistance of nickel alloys to localized corrosion (pitting, crevice corrosion) but there is remarkably little quantitative information, particularly for extended exposure periods. Several sets of data obtained from immersion corrosion experiments in the Panama Canal Zone (Figure 12) (Southwell and Alexander 1967) are shown in Figure 12 for commercially pure nickel, two types of Monel and for 70:30 copper–nickel. Both the average depth of the 20 deepest corrosion pits observed on the four surfaces of the two coupons recovered at each time point are shown (Figure 12a), as well as the observed depth of the deepest pit (Figure 12b). For all four alloys it is clear that the maximum values of the average depth of the 20 deepest pits are obtained within the first two years, and that there is then essentially no increase in that average depth (Figure 12a). A similar remark applies to value of the deepest pit depth observed at various time points—the deepest pit depth is obtained within the first two years. Thereafter, for the next 14 years or so, there is, apart from scatter in the depths of pits observed for different coupons,

Figure 10: Corrosion loss of commercial pure nickel over 20 years exposure at the industrial US mainland exposure site at Bayonne, NJ.

Figure 11: Corrosion loss of commercial pure nickel over 20 years exposure at several different industrial exposure sites in the US.

no change in the depth of the deepest pit. Of course this is not to say that other, i.e. more, pits will have reached a similar depth with continued exposure. The trends for localized corrosion shown in Figure 12 show no evidence of bimodal characteristics.

Maximum pit depth data for immersion corrosion at about 1750 m depth and for marine sediments in the Pacific Ocean off California, mostly for exposure periods up to one year, but some for up to three years, are available (Reinhart 1976). Only the depths of the deepest pits are reported. Examples are shown in Figure 13 for the three-year exposure data. Evidently the maximum pits depths increase over the first 2–3 years, converging to about 1.25 mm, with considerable scatter. Despite the large differences in depth

and in seawater DO, the trends are not inconsistent with the convergence of maximum pit depths shown in Figure 12. Generally similar behavior can be seen for Monel immersed in freshwater (Figure 14) but with much slower convergence to a maximum pit depth of about 1.25 mm.

6 Discussion

Irrespective of the precise exposure conditions, the trends derived from the data for mass loss (corrosion loss) as presented herein for longer-term exposures of a variety of nickel alloys, all appear to be consistent, often closely, with the bimodal model (Figure 1). This is despite the scale

Figure 12: Corrosion pit depth for several nickel-copper alloys under seawater exposures, showing (a) data and trends for the average of the 20 deepest pits and (b) data and trends for the maximum of the observed pit depths (data from Southwell and Alexander 1967).

Figure 13: (a) Examples of growth in depth of crevice corrosion for three different corrosion-resistant Ni alloys. Page numbers refer to location in the report by Reinhart (1976) (b) Growth of localized corrosion for pure nickel in seawater (data from Reinhart 1976).

Figure 14: Gradual development of corrosion pit depth of Monel exposed in tropical fresh water for up to 16 years.

for the horizontal axes and often also the vertical axes being considerably different in magnitudes represented. In most cases the computer-generated trends are very close in topology to the trend of the bimodal model when the trends are anchored to the observed data points. In some cases a degree of subjective interpretation between the anchor points permitted a closer development of the bimodal trend.

In some cases the data sets, such as those extracted from the deep-sea experimental work reported by Reinhart (1976), showed inconsistencies, for example with successive corrosion losses decreasing with increased exposure

period (e.g. the trends at right of Figures 5a and 6a). Fundamentally this cannot be correct for the one piece of metal being corroded. Corrosion is a 'positive-definite' process. Even positive-semidefinite, implying periods of no increase in corrosion with increasing exposure period is, from a physico-chemical point of view, extremely unlikely. But even in these cases there usually was evidence of an underlying bimodal trend.

One possible reason for the inconsistencies from one experimental campaign might be as follows. Typically, the experiments used coupons and, typically also, these are isolated from each other, but usually are in quite close proximity, mounted on exposure racks within a very large sub-sea facility. Much experience with exposure of coupons has shown that the corrosion losses between them usually are very consistent. As noted, for mild steel in seawater at the same exposure location the typical coefficient of variation for mass losses between coupons is around 0.05 (Melchers 2003b) but it also has been observed that coupons located near the edge of a rack, possibly adjacent to structural or support elements, often have a lower mass loss. An example of this was for 90:10 CuNi alloys already after only one year exposure in seawater, with the coupon at the very side of the exposure rack having corroded slower and somewhat differently (Melchers 2015). It is not possible now to back-track to attempt to ascertain the potential cause(s) of the inconsistencies, but it is reasonable to accept that they are not the result of random variability in corrosion between the coupons but rather the result of experimental influence(s). There is another possibility, namely that the analyst overlooked dividing the mass loss between the two sides of the coupons for the coupons at some exposure

times in Figures 5a and 6a (so as to give, for example, the ‘alternate’ curves shown). Even though it is a common mistake, it may be considered less likely because it would have had to be made for multiple cases. This is not evident in the available data. Irrespective, it is clear that with or without correction for what are, in just a few cases, some inconsistencies in the data, all the trends are bimodal, most often without any need for interpretation.

All the mass (corrosion) loss trends show the presence of a first mode and a second mode, idealized as separated at time t_a (Figure 1). For immersion in tropical (27 °C mean temperature), almost fully aerated surface waters (Figures 2 and 3) t_a is in the range 2–3 years while in the deep sea exposure conditions it is much lower—about 0.6–1.0 years and slightly longer for alloy N04408 (Figure 6b). This is to be expected on the basis of the deep-sea waters having much lower DO content (Reinhart 1976). The strong effect of DO on corrosion, and in particular on parameters t_a , c_a and r_o (Figure 1) has been demonstrated experimentally, at least for steel, with all three declining with reducing DO (Melchers and Chernov 2010). It is for this reason that the bimodal characteristic was revealed already within the three-year exposure period for the deep-sea experiments.

It would appear that the best data available for long-term observations of pit depths is that from the Panama Canal Zone experiments (16 years), obtained from the two sides of duplicate coupons, with the maximum pit depths and the averages of the 20 deepest pits reported (Schumacher 1979; Southwell and Alexander 1967). Figure 12 shows the data as a function of exposure period. In the high temperature (27 °C average) seawater pit depths grow rapidly in the first 1–2 years and slightly slower for hot-rolled Monel and 70:30 CuNi. The decrease in recorded pit depth with increased exposure period, as shown in Figure 12, most likely is the result of measurements being made to the corroded surface rather than the original surface (Southwell and Alexander 1967). This usually is inevitable as in most cases for longer-term exposures the original surface will have become corroded and thus no longer available as a reference. Despite this, it appears that all the trends have stabilized with increased exposure, although a slightly increasing trend relative to the original surface cannot be ruled out. One aspect is the possibility of a reduction of electrochemical potential for pit growth as nickel-related corrosion products build-up, in a manner parallel to that for steels. This is also a matter for further investigation.

The trends in the growth of pit and crevice corrosion are perhaps best illustrated for the low seawater temperature, low DO, seawater of the deep-sea exposures. Figure 13 shows four such trends, three for nickel alloys and one for

almost pure Ni. These all follow a slower development than the Ni alloys in warmer waters with higher DO. The trends show a roughly linear progression to a maximum pit depth of 1.25 mm, similar to that for most cases shown in Figure 12. However, a different interpretation for those in Figure 13a is to visualize the trends as step-wise, increasing from zero to about 0.3 mm, then to about 0.75 mm and then to about 1.2 mm. The trend in Figure 13b is less clear but could be interpreted similarly. The observation periods in Figure 14 are spaced too far apart to make similar inferences. Although not previously noted for nickel alloys, step-wise trending for pit depth development (and by implication development of depth of crevice corrosion) has been observed for mild steel (Jeffrey and Melchers 2007), cast iron (Asadi and Melchers 2018), high alloy steel (Melchers and Ahammed 2018) and less directly for corrosion of welds between steels (Chaves and Melchers 2011). From a theoretical viewpoint it would be of interest to ascertain whether the nickel alloys do indeed show such incremental steps in the development of pitting and crevice corrosion.

The possibility of MIC in the corrosion of nickel alloys has been considered (Little et al. 1990) but remains unclear (Little and Lee 2007). Nickel alloys are susceptible to biofouling, as noted, for example for the seawater immersion and tidal exposures at the PCZ test sites, for which it was proposed that attachment of fouling organisms, including barnacles, promoted localized corrosion, including pitting corrosion that reached some 0.6–1.2 mm deep in the first year or so, and up to 1.5 mm deep after 16 years (Schumacher 1979). However, Ni–Cr–Mo alloys appear to be less prone to micro- and macrofouling attack, particularly under higher flow conditions (>1.5 m/s) (Davis 1998). These matters also could benefit from further investigation as to their effect on longer term corrosion.

One set of alloys not considered herein is the nickel aluminum bronzes (NAB). These are essentially copper alloys, typically with 5% wt. Ni. They are used widely in submarine seawater cooling systems because of their superior strength and shock resistance, and reasonably good corrosion resistance. Field observations indicate that some NAB alloys remain free from marine organisms for at least for two years of seawater exposure (Wang 2008). Unfortunately, data for longer-term corrosion loss or pit depth of NABs appear unavailable in the open literature, although it is understood that (classified) reports exist with data for up to three years exposure in colder and in tropical waters (Stokes et al. 2007). This aspect also could be explored further, perhaps through independent tests.

While the ‘power’ law has long been claimed to be appropriate for the, perhaps slightly approximate,

representation of the development of corrosion loss with time, it is clear even from a superficial examination of the trends in Figures 1–11 that none of the data sets for corrosion mass loss is consistent with such a simple function. The only possibility is that it might be used as an approximation for the development of corrosion mass loss in phases 1–2 in mode one of the bimodal trend (see Figure 1). Indeed this would appear to be an appropriate approximation for data sets of limited exposure periods (i.e. $t < t_a$). Similar comments apply to pit depth as seen in the examples in Figure 12.

Overall the results of the analyses presented herein add a degree of unity in corrosion characteristics across a range of alloys, now including nickel alloys, with all exhibiting bimodal behavior for corrosion loss and, for localized corrosion, generally similar patterns of a fast increase in pit or crevice depth for some time, followed by a much slower rate of development later. Apart from clearly indicating for both mass loss and for depth of localized corrosion that there are changes in corrosion behavior as corrosion develops with time, the present results reinforce the notion that there are inter-relationships between the overall mass (corrosion) loss behavior and the detailed development of depth of localized corrosion particularly for longer term exposures. There is some evidence for steels that the growth, development and agglomeration of pits are instrumental in the development of mass loss (Jeffrey and Melchers 2007), more generally the precise mechanisms involved, including for other alloys, remains a matter for further investigation. However, it is now clear from the present observations for the development of corrosion mass loss and for localized corrosion for nickel alloys that the linkages in behavior between them are not limited to the exclusive domain of one or other alloys, but rather to be similar for a range of alloys. Unravelling these issues represents an exciting set of challenges for future research.

7 Conclusions

Based on the reinterpretations of published exiting data summarized here, the following conclusions may be drawn:

- (1) Where the data are coherent and sufficiently extensive and detailed in time, the trends for mass- (corrosion-) loss of the various high nickel alloys considered herein largely are consistent with a bimodal characteristic, irrespective of exposure environment, and are generally similar to what has been observed for several other alloys.

- (2) The development of the depth of localized corrosion such as pitting or crevice corrosion for high nickel alloys occurs relatively quickly for the first few years of exposure and then declines significantly to what appears to be an almost uniform, low rate, at least for the most extended periods of exposures (up to 16 years) considered herein.
- (3) The topological similarity in terms of the bimodal trend for corrosion loss and also, separately, for the trend for the development of pit or crevice depth with increased exposure period have parallels in the corrosion behaviour of several other alloys. This suggests that there are similarities in the underlying mechanisms and also between the mechanisms involved, including for nickel alloys.
- (4) The present interpretations of existing data sets reinforce the notion that also for nickel alloys extrapolation from shorter-term observations of corrosion loss or maximum pit depth usually is not appropriate for the prediction of longer-term corrosion such as typically important for practical infrastructure applications.

Acknowledgments: The author acknowledges the useful discussions with Drs. Robert Jeffrey and Igor Chaves.

Author contribution: The author has accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: The author acknowledges the support of the Australian Research Council under grant DP130104410.

Conflict of interest statement: The author declares no conflicts of interest regarding this article.

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