

# Bi-modal trends in the long-term corrosion of copper and high copper alloys



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## ABSTRACT

The evolution of corrosion loss and maximum pit depth of copper and copper alloys exposed for long periods of time in natural and industrial environments is shown to be more consistent with a bi-modal functional form than with the classical power law. Data from several long-term exposure test programs supports this proposition. The bi-modal behaviour signals a change from mainly cathodic oxygen reduction to a subsequent transitory corrosion process that may be modelled as involving pitting under earlier copper corrosion products. Possible reasons for some data sets showing decreasing maximum pit depths with increasing exposure time are discussed.

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## 1. Introduction

Copper and in particular high copper alloys such as copper nickels and certain brasses are used extensively in marine applications for piping, tubing, condensers and heat exchangers and, at one time, for sheathing the hulls of timber ships, largely because of their high resistance to corrosion and their good resistance to bio-fouling [1,2]. Copper as an exterior casing to a carbon steel lining has been proposed for containers for nuclear wastes buried in deep geological repositories and exposed to ground-waters [3]. Copper has a record of excellent corrosion resistance in atmospheric exposure conditions [4,5]. As a major component of bronzes, copper has a particularly long history of use in art [6] and is of much interest to archaeologists and museum curators [7].

There has been more than a century of scientific study of the corrosion of copper, particularly in relation to its behaviour in seawater and in sulphur dioxide contaminated atmospheres [5,6,8]. In chloride environments early investigations [9,10] identified the corrosion products formed on copper to consist of mainly of cuprous oxide ( $\text{Cu}_2\text{O}$ ), cuprous chloride ( $\text{CuCl}$ ) as well as other products including cupric hydroxide  $\text{Cu}(\text{OH})_2$ , cupric oxide  $\text{CuO}$  and to a lesser extent, mainly in the outer layers of the corrosion product, the loosely adherent precipitation products atacamite ( $\text{Cu}_2(\text{OH})_3\text{Cl}$ ) and malachite ( $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ ) [11]. The dependence of these products on pH and electrochemical potential has been summarised in Pourbaix diagrams for the ( $\text{Cu}$ ,  $\text{H}_2\text{O}$ ,  $\text{Cl}^-$ ) system [12,13] with inclusion also of carbonate and bicarbonate ions as necessary for

real seawaters (since these usually are carbonate–bicarbonate saturated). This pH dependence applies both for very short-term corrosion but also for longer term exposures. For example, compared to copper corrosion in 3%w/v NaCl solutions, the buffering capacity of seawater and the saturation of carbonates tend to lower the rate of  $\text{Cu}_2\text{O}$  production and to increase the production of cuprous complexes. The effect is to produce higher corrosion in (non-stagnant) seawater compared with simple saline solutions [14]. Also, for exposures up to about 90 days, there appeared to be negligible effect caused by the concentration of dissolved oxygen, which suggested that oxygen diffusion was not the rate-controlling mechanism for these exposure periods. On the other hand, there can be considerable differences in corrosion response between short term and long term exposures, for example as has been noted for 90:10 copper–nickels under the same environmental exposure conditions [15,16]. It follows that understanding of the corrosion behaviour of copper alloys for long-term service may not necessarily be available from short-term observations.

Long-term corrosion behaviour both for mass loss and for maximum pit depth as a function of exposure time is relevant for the estimation of future life or remaining life of infrastructure [17]. Traditionally, and particularly for atmospheric corrosion, it was assumed that the power law, derived originally by Tammann [4] in 1923 for copper roofs and used empirically for steels in 1934 [18] could be used to describe the progression of mass loss as a function of time, both for short-term (days, weeks) and for long-term (decades) exposures. However, already in 1968 Hummer et al. [19] observed the poor fit of the power law to data for long-term corrosion of copper.

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More recently it has been shown that in a variety of exposure conditions including marine, freshwater and various atmospheric environments the data for corrosion loss (and also maximum pit depth) typically follows a characteristic bi-modal functional form (Fig. 1). This has been found to be the case for a variety of steel types including low-alloy and copper-bearing steels, weathering steels and the more common grades of chromium-bearing or stainless steels [20]. It also applies to cast iron [21] and recently has been shown to apply also for corrosion loss and for maximum pit depth for a variety of aluminium alloys [22]. The bi-modal functional form has been modelled as a sequence of consecutive phases, each representing a corrosion rate controlling process. They are shown in Fig. 1. The main parameters that describe each phase have been calibrated to field data for low-alloy and copper-bearing steels continuously immersed in normal, unpolluted coastal seawater [20]. The effects of various environmental parameters including nitrogenous water pollutants [23] have been considered.

The present paper is concerned with the extent to which the bi-modal trend is valid for the corrosion of copper and high copper alloys in long-term exposures, mainly in marine exposure conditions and also in some other natural and industrial environments. As in the earlier work, the analysis proceeds with the working hypothesis that the bi-modal function is applicable. This means that it is assumed that the underlying physico-chemical processes governing corrosion are assumed given, in conceptual form (see Fig. 1), and must be calibrated to suitable and relevant data. Corrosion observations that form the data items should be considered samples from the underlying physico-chemical processes and as such are prone to uncertainty. In some cases it is possible for the data to be in error. Importantly, the data themselves are but part of the information available. They do not by themselves define the model. Therefore an approach based on curve-fitting to determine a model is considered not acceptable. On the contrary, the present approach permits the introduction of prior knowledge and of understanding of the development of the corrosion process and the effect of corrosion products on the diffusion processes involved in that process [20]. An important part of this is the knowledge that some other metals and alloys already have been shown to follow the bi-modal functional form.

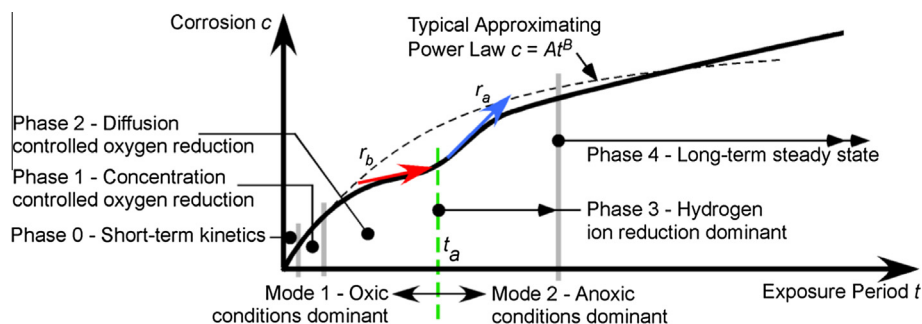
In the next section data reported in the literature for copper corrosion loss are used and where necessary re-interpreted to show that for marine immersion, tidal, marine coastal, fresh water and inland atmospheric corrosion environments and some industrial environments the bi-modal model is appropriate in the majority of cases. The same approach is taken for the very limited data available for pitting corrosion. The reasons for the persistent observation of the bi-modal trend are then discussed. Attention is given also to why the bi-modal behaviour is (almost) absent in the case

of (commercially) pure copper in fresh water with very low ion contents and also in some atmospheric exposure environments. Finally, an explanation is proposed for the apparently anomalous observations that for pitting in some cases the maximum depth of pitting appears to reduce with increasing exposure period.

## 2. Corrosion loss data and trends

### 2.1. Data sources

Most investigations of the corrosion behaviour of copper and copper alloys have focused on short-term laboratory trials, electrochemical testing, examination of corrosion products, or relatively short field exposure programs [8,24], [25]. There are some exceptions, including the 20 year study of atmospheric corrosion for a range of almost pure coppers from various manufacturers exposed to 3 different atmospheric environments [26,27]. In this test program, commenced in 1932, the total coupon mass, including corrosion products was measured at 1, 2, 3 and 5, and the mass of cleaned coupons only at 8, 10 and 20 years exposure. Using the assumption that all copper lost to corrosion was converted to corrosion product ( $\text{Cu}_2\text{O}$ ) and thus included in the measured mass, produced, after allowing for the relative molecular masses, overestimates of the loss of metal for years 1, 2, 3 and 5. More difficult was the data for the test program of various copper alloys [28,29] apparently commenced in 1927. In this test program, the total coupon mass, including corrosion products was measured at 1, 2, 3, 5, 8 and 10 years, and the mass of cleaned coupons only at 10 and 20 years exposure. Because some coupons showed mass increases (as a result of corrosion product) and since it is not known how much of the metal loss was lost to the environment rather than being converted into adherent corrosion product, it was found not possible to derive reasonably accurate estimates of metal mass loss from the results reported for 1, 2, 3, 5 and 8 years exposure. As a result, this data was disregarded. Another long-term test program [30] for the atmospheric corrosion of copper alloys took observations only at a small number of points in time, insufficient for use herein. The most extensive set of corrosion loss and pit depth data for copper and copper based alloys was found to be those obtained in the 16 year exposure experiments in the Panama Canal Zone (PCZ) conducted in the period just after the Second World War when it was realised that there was very little data for corrosion in tropical climates [19,31]. In this work observations were made at 1, 2, 4, 8 and 16 years of exposure from which mass loss, maximum pit depth and the average of the 20 deepest pits (from 4 faces of duplicate coupons) were derived. This program also reported data for a variety of copper alloys. Table 1 summarises the alloys considered herein and Table 2 the exposure conditions.



**Fig. 1.** Bi-modal corrosion loss model showing phases 0–4 with a summary description for each, together with the parameter  $t_a$  dividing the predominantly aerated (oxic) mode (phases 0–2) from the predominantly de-aerated (anoxic) mode (phases 3 and 4). The instantaneous corrosion rate  $r_b$  near the end of phase 2 and just before reaching  $t_a$  changes to  $r_a$  thereafter, that is, near the beginning of phase 3.

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