

# Temperature Effect on Seawater Immersion Corrosion of 90:10 Copper-Nickel Alloy

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## ABSTRACT

*There are apparently conflicting observations about the influence of seawater temperature on the immersion corrosion of copper-nickel alloys, with both increases and decreases in temperature having been observed. During the 1980s, ASTM sponsored a worldwide corrosion study, which included 90:10 copper-nickel (UNS C070600). At first sight there is no order in the results regarding the effect of seawater temperature. However, when the results are examined in detail, allowing for water velocity and environmental conditions and carefully considering the implications of previous laboratory and field studies, some order can be obtained. This shows that a relationship between corrosion and temperature in the range of 10°C to 40°C can be proposed, which is consistent with previous observations.*

**KEY WORDS:** *copper-nickel alloys, field trials, immersion testing, laboratory trials, seawater, temperature, velocity, weight loss*

## INTRODUCTION

The corrosion of copper-nickel is of interest for a number of applications, including piping for desalination plants and cladding for vessels. The first typically involves high water temperatures and velocities.

The second involves a more moderate range of temperatures and velocities. Of main interest has been 70:30 and 90:10 copper-nickels. The present paper is concerned only with 90:10 copper-nickel (UNS C70600)<sup>(1)</sup>.

The corrosion characteristics of copper-nickel alloys have been summarized in a number of review articles.<sup>1-2</sup> It appears that the influence of temperature on corrosion is not well-understood, with increasing, decreasing, and no effective changes having been reported with increasing temperature and over apparently conflicting temperature ranges.

Detailed laboratory studies of temperature effects and velocity for 90:10 copper-nickel have been reported.<sup>3-5</sup> Rotating cylindrical electrodes (RCE) were used to determine instantaneous corrosion rates at 20°C and 40°C in natural seawater using impedance resistance measurements and polarization techniques. Reported average corrosion rates were obtained from weight loss experiments extending over 36 to 70 days for 18-mm diameter, 120-mm long pipe samples. Other relevant observations are available, such as for the effect of sulphides (usually obtained as a by-product of other investigations).<sup>6</sup>

A long-term (7-year) field trial on 90:10 copper-nickel was reported by Efir and Anderson.<sup>7</sup> They found that, for immersed specimens exposed to constant 0.6 m/s velocity, the total corrosion was always considerably greater than for specimens exposed to quiescent tidal conditions. Notably, the initial corrosion rate for the high-velocity samples was three to four times that of the quiescent samples. Despite this, the eventual longer term instantaneous corro-

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<sup>(1)</sup> UNS numbers are listed in *Metals and Alloys in the Unified Numbering System*, published by the Society of Automotive Engineers (SAE) and cosponsored by ASTM.

sion rate (i.e. that after several years of exposure) was almost identical at 1.3  $\mu\text{m}/\text{y}$ .

A number of other reports have been given regarding the corrosion behavior of 90:10 copper-nickel (e.g., Parvizi, et al.<sup>2</sup>). Some of these will be referred to in the discussions to follow. Unfortunately, a number of others were found to lack sufficient details of the experimental conditions to allow use of the reported data in the present investigation. This applies particularly to factors such as velocity, salinity, and oxygenation.

In the next section of this paper, an overview is given of the results of the ASTM worldwide immersion corrosion study along with a summary of environmental and other conditions pertaining to each sampling site. The following section presents inferences and observations drawn from data previously reported in the literature. Specifically, the emphasis is on the effect of velocity and of temperature on the short-term corrosion-time behavior and the effect this may have on longer-term behavior. These observations are used to interpret the ASTM data and, on that basis, to propose a relationship for corrosion as a function of temperature and exposure duration.

## WORLD-WIDE EXPOSURE STUDY

An important source of data is the ASTM sponsored worldwide "round robin" test program conducted during the 1980s and reported on by Phull, et al.<sup>8</sup> In this program, standard 300 by 100 by 6 mm immersion specimens of copper-bearing mild steel (UNS K01501), 90:10 copper-nickel, and aluminum (UNS A95086) were recovered at 0.5, 1, 3, and 5 year intervals at 14 different locations around the world, but mainly in the northern hemisphere and in temperate regions. For convenience, the results for weight loss of the 90:10 copper-nickel samples are summarized in Appendix A, and details of the sites and reported environmental conditions are summarized in Appendix B. As part of the present work, an attempt was made to refine the information about local conditions, including environmental conditions, and this has been added in Appendix B.<sup>9</sup>

An important observation from Appendix A is that, after some initial period, in nearly all cases total corrosion is a linear function of time, at least for the exposure period reported (5 years). Where serious deviations from linearity occur, there appear to be reasons such as unusual exposure conditions (e.g., California and Hawaii), as can be seen from the notes in Appendix B.<sup>9</sup>

## WATER VELOCITY

It seems reasonable to assume that the seawater velocity at the various sites in the ASTM study in most cases was rather low. The exceptions are CA,

where water velocity and wave action was specifically recorded as being high;<sup>8,10</sup> FL, where conditions have been described previously as particularly "quiet-cent";<sup>11</sup> and IT, where the samples were suspended at a shipping dock in a rather enclosed harbor (Appendix B).<sup>12</sup> In all other cases the samples were exposed to wave action at the depth of specimen location. From observations of sea conditions and from inspection of several sites, it is unlikely that the water velocity would have exceeded 0.05 m/s for more than a small portion of the time, and for much of the time it would be considerably less. It might be noted that most sites involved some degree of protection from severe wave action and tidal conditions although local eddy currents, such as those formed by obstructions (e.g., piles), could have been a factor. Unfortunately, apart from those mentioned above and those shown in Appendix B, there are no recorded field observations.

Water velocity as a factor in the corrosion of copper-nickel has been studied extensively in laboratory experiments.<sup>13</sup> Many of these deal with "impingement" corrosion, which is only of peripheral interest for the present discussion. Others provide laboratory observations of rotating disc electrodes or rotating spindles. The information from these is difficult to translate to field conditions. However, observations involving RCE and pipeflow experiments are more easily interpreted. Some of these were used to estimate the effect of temperature and velocity.

Thus, IJsseling (Figure 9 in Reference 3) reported that, at 20°C and at very early exposures, there was a very distinct water velocity effect on "uniform" or general corrosion of copper-nickel, with the instantaneous corrosion rate as measured by linear polarization resistance ( $R_p^{-1}$ ) being about 350% to 400% greater at 1 m/s than the corrosion rate at zero velocity.<sup>3</sup> Since this was measured in short-term exposed tube specimens, the corrosion rate was likely governed by concentration polarization (e.g., Jones<sup>14</sup>). This means that the rate of oxygen diffusion and hence the corrosion rate (that is, the current density  $i$ ) is controlled (or limited) by the thickness of the diffusion boundary layer  $\delta$  or:

$$i = i_L = \frac{D_H n F C}{\delta} \quad (1)$$

where  $i_L$  is the limiting current density,  $D_H$  is the diffusivity of the hydrogen ions in water,  $n$  is the number of electrons exchanged in the reaction (= 4 here),  $F$  is Faraday's constant, and  $C$  is the solution concentration. The latter four factors are constants for a given immersion situation. Hence, Equation (1) may be written as  $i = a/\delta$  where  $a$  is a constant.

From fluid dynamics it is known that the thickness of  $\delta$  is an inverse function of water velocity  $v$ . Russian research (e.g., Chernov<sup>15</sup>) has suggested that

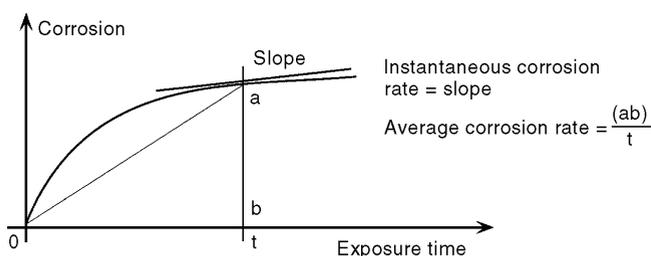


FIGURE 1. Definition of instantaneous and average corrosion rates.

an empirical relationship of the following general form has been found to fit well with field observations:

$$\delta = \frac{d}{b + c\sqrt{v}} \quad (2)$$

where  $b$ ,  $c$ , and  $d$  are constants. Combining Equations (1) and (2) it follows that:

$$\frac{dc}{dt} = i = A + B\sqrt{v} \quad (3)$$

where  $dc/dt$  is the instantaneous corrosion rate (i.e., the slope of the corrosion-time [ $c - t$ ] curve), and  $A$  and  $B$  are constants.

The data reported by IJsseling in his Figure 9 appears to fit this relationship very well.<sup>3</sup> Converting  $1 R_p^{-1}\Omega^{-1}\text{cm}^{-2} \times 10^{-6}$  to  $0.385 \mu\text{m}/\text{y}$  as suggested for this data, it is easily shown that:

$$\frac{dc}{dt} = 60 + 200\sqrt{v} \mu\text{m} / \text{yr} \quad (4)$$

for  $v < 1$  m/s. This relationship will remain valid for relatively low velocities, that is until  $v$  becomes sufficiently large to create a turbulent boundary layer that exerts a shear stress  $\tau$  sufficient to remove corrosion product:<sup>16-17</sup>

$$\tau \propto v^2 \quad (5)$$

The literature appears to contain few detailed observations of the effect of higher water velocity on immersion corrosion of copper-nickel. An upper bound on various 85-day observations of material loss in natural seawater flowing through a nonrecirculating 2-in. polyvinyl chloride pipe system was reported by Gudas and Hack.<sup>6</sup> The bound on average corrosion rates  $\bar{c} = (\Delta c/\Delta t)$  as a function of velocity, over the range 1 m/s to 6 m/s, has a form consistent with Equation (5) and can be represented approximately by:

$$\bar{c} = 9.2v^2 + 40 \mu\text{m} / \text{yr} \quad (6)$$

Since the corrosion rate of copper-nickel over the exposure period for these tests (85 days at  $\sim 20^\circ\text{C}$ ) is high and approximately linear, the average corrosion rate can be taken roughly as directly proportional to total weight loss  $c$ . It follows that, for these observations, the total corrosion (material loss) becomes:

$$c \propto v^2 + \text{constant} \quad (7)$$

Differentiating Equation (7) provides the instantaneous corrosion rate:

$$\dot{c} = \frac{dc}{dt} = \text{constant} \times 2v \quad (8)$$

since  $dv/dt = \text{constant}$  for constant flow rates.

Laboratory test results described by Syrett and Wing for 90:10 copper-nickel generally agree with these deductions although they used a recirculating system including water filtration.<sup>18</sup> This could have had an effect on the possible influence of marine organisms on corrosion behavior. They found that the 230 h (9.6 day) instantaneous corrosion rate, (i.e.,  $\dot{c} = dc/dt$ ) was essentially linear with increasing velocity, at least for  $v > \sim 1$  m/s. This is consistent with Equation (8). For lower velocities the instantaneous rate was lower than the linear trend, suggesting consistency with Equation (5) although, because of the lack of detail provided and potential experimental error, no firm conclusions can be drawn.

In general, the instantaneous corrosion rate (i.e., the slope of the  $c - t$  curve) changes more rapidly than the average corrosion rate (Figure 1). Evidently, unless the corrosion rate is constant, the instantaneous corrosion rate generally can differ significantly from the average rate. For very short-term exposures, the instantaneous rate will be greater than the average. This is demonstrated in Table 1 where both the Gudas and Hack tests<sup>19</sup> and the Syrett and Wing results<sup>18</sup> are converted to total corrosion loss at 85 days' exposure. As noted, both experiments were conducted at  $\sim 20^\circ\text{C}$ .

For the present observations, it is evident that, since the difference between the corrosion rate measures is not large for early corrosion (since the corrosion rate does not depart greatly from constancy), a rough comparison can be seen between the two sets of results. This suggests that the theory sketched above is compatible with the limited experimental observation currently available.

IJsseling's experimental observations predate both of the above observations but are not mentioned by either.<sup>3</sup> It is difficult to compare his results for  $v < 1$  m/s with the above since the period of exposure of specimens is not reported, except that they were on "newly inserted" test tubes (in a nonrecirculating test system using natural seawater). However, some simple comparisons can be made. Although the

TABLE 1

Estimated Total Corrosion at 85 Days' Exposure at Velocities to 5 m/s

Velocity (m/s)	Gudas and Hack <sup>19</sup>		Syrett and Wing <sup>18</sup>		
	Average Corrosion Rate $\bar{c} \mu\text{m} = (\Delta c/\Delta t) \mu\text{m}/\text{y}$	Total Corrosion ( $\mu\text{m}$ )	Corrosion "Rate" After 230 h ( $\mu\text{g}/\text{m}^2$ )	Instantaneous Corrosion Rate $dc/dt$ ( $\mu\text{m}/\text{y}$ )	Total Corrosion ( $\mu\text{m}$ )
0	40	9.2	—	—	—
1	50	11.6	15	65	15.1
2	85	19.8	30	130	30.3
3	130	30.3	40	170	39.6
4	190	44.3	60	260	60.6
5	270	62.9	75	325	75.7

TABLE 2

Comparison of Laboratory and Field Observations for Total Corrosion Under Different Velocity Conditions

Exposure	IJsseling <sup>3</sup> Observed $R_p^{-1}$ <sup>(A)</sup>	Short-Term Exposure Corrosion Ratio	Efird and Anderson <sup>7</sup> 1-Year Ratio <sup>(B)</sup>	3-Year Ratio <sup>(B)</sup>	5-Year Ratio <sup>(B)</sup>	7-Year Ratio <sup>(B)</sup>
Quiet (tidal)	150	1	1	1	1	1
0.6 m/s (constant)	550	3.7	2.85	2.9	2.95	2.7

<sup>(A)</sup> Proportional to instantaneous corrosion rate.<sup>(B)</sup> Average corrosion rate obtained from weight loss measurements.

IJsseling observations were made on tube specimens, it is not inappropriate to compare these with flat specimens exposed to tidal conditions with water velocity parallel to the specimens.

Efird and Anderson reported such (long-term) observations for specimens exposed at the LaQue Centre at Wrightsville Beach, NC.<sup>7</sup> One set of specimens was mounted vertically off the laboratory wharf in quiet but tidal seawater, in conditions generally similar to those for the later ASTM tests. The other set of specimens was exposed to seawater flowing with a constant velocity of 0.6 m/s through a specially constructed trough. The average water temperature was ~ 20°C. A comparison of total corrosion for these specimens over various periods of exposure is given in Table 2, along with the instantaneous short-term corrosion rate and the total corrosion estimated from IJsseling's experiments.<sup>3</sup>

It is evident from the results in Table 2 that the ratio for velocity effect reduces slowly with length of exposure. Recognizing the difference between the corrosion rate definitions shown in Figure 1, it can be concluded also that the "quiet tidal" exposure condition under the laboratory wharf at Wrightsville Beach, NC, represents conditions much less than 0.6 m/s  $v$  on average. Thus, at Wrightsville Beach, the effect on corrosion of water velocity for the specimens exposed to tidal immersion conditions can be considered to be low to very low when seen also in the context of other information about the effect of velocity on corrosion rate.

Since the ASTM specimens at the Wrightsville Beach laboratory wharf were exposed in a generally

similar way and in the same location, generally similar conditions and hence effects on corrosion would be expected to prevail for the ASTM specimens.

Subjective judgment suggests that, except for the sites in CA, FL, and IT (Appendix B), the water velocity at the other sites in the ASTM series was not substantially higher than that at Wrightsville Beach. This suggests that water velocity, and hence its effect, was comparable between the ASTM sites.

An important laboratory observation is that at 40°C there was no noticeable velocity effect, at least for velocities in the range of 0 m/s to 1 m/s.<sup>3</sup> This was attributed to the very rapid formation of a protective and robust corrosion product layer at this temperature. This did not occur at 20°C for the short-term exposure time. Moreover, the long-term observations reported by Efird and Anderson (at ~ 20°C) show that, for both quiet tidal and the constant 0.6 m/s exposure conditions, the corrosion rate took several years to reach a steady-state condition.<sup>7</sup> This suggests that it took this long for a sufficiently protective corrosion product layer to form. Importantly, it took longer for this to occur at higher velocity (7 years compared to 3 years).

IJsseling's observation at 40°C is supported by polarization resistance measurements.<sup>3</sup> These show a very rapid drop after only a few days' exposure at 40°C. It took longer for this to occur at lower temperatures. The importance of this observation lies in the conclusion that, for temperatures ~ 40°C, a protective and stable corrosion product forms quickly. As a result, there should be only a slight increase in total corrosion with time thereafter.

In view of the above observations, it is proposed that the longer-term effect of velocity on corrosion-time relationships is that observed by Efirid and Anderson, namely, that the development of a protective corrosion product layer is delayed in time with greater velocity.<sup>7</sup> This means that the instantaneous corrosion rate soon after immersion (and subsequently) is higher for higher velocities (as would be expected). It follows that the longer-term  $c - t$  curve is higher in direct proportion, at least until the corrosion product layer becomes stabilized, at which time the corrosion rate also stabilizes. This stabilized value is then uniform ( $\sim 1.3 \mu\text{m}/\text{y}$  at  $\sim 20^\circ\text{C}$ )<sup>7</sup> and independent of earlier behavior. It follows that simple multipliers to allow for velocity effects, without consideration of the duration of exposure, can have validity only during the early period of exposure. This is supported by the results shown in Table 1.

The instantaneous corrosion rate becomes steady when there is equilibrium between corrosion product removal as a result of shear stress and turbulence, and its replacement by metal oxidation as permitted by oxygen rate supply through the corrosion product layer. This scenario matches models previously sketched for corrosion product behavior for copper and copper-nickel alloys.<sup>2,16,18</sup>

## SHORT-TERM TEMPERATURE EFFECT

It is reasonable to assume that the possible effect of water velocity is sufficiently similar to be taken as a consistent influence for all the ASTM sites (with the exception of CA, IT, and JA). Clearly, this is not to suggest that there is no velocity effect but only that it is comparable. It will be taken as sufficient to describe the possible velocity effect as that attributable to "at sea" immersion conditions. This will include localized velocity effects resulting from wave action.

To interpret the ASTM data, it is useful to consider laboratory observations by IJsseling and coworkers on the short-term behavior of 90:10 copper-nickel.<sup>3-5</sup> They found that instantaneous corrosion as measured by polarization resistance measurements depended very much on water temperature, as shown schematically in Figure 2. These plots indicate that the initial corrosion rates may be low but can very rapidly rise to high values and then decline at a rate which appears to depend on the water temperature (see also Gudas and Hack<sup>6</sup>).

Not all plots show the very steep early rise in corrosion rate, presumably because of experimental limitations. However, such a rise is consistent with the possibility of a very short period after immersion during which time conditions on the metal surface are changing rapidly as corrosion becomes established.

An important observation is that the instantaneous corrosion rate drops very rapidly within about 4 days after exposure from its high peak rate to a very modest rate for  $40^\circ\text{C}$  water temperature, and the drop-off becomes less as the temperature is reduced, step-wise, to 30, 20, and  $10^\circ\text{C}$ .<sup>4</sup> These were the only temperatures considered in the experimental work of IJsseling, et al.<sup>4</sup> Comparison to later experiments shows a generally similar pattern, except that there is rather wide variation in the peak instantaneous corrosion rates, particularly at  $20^\circ\text{C}$ .<sup>5</sup>

The instantaneous corrosion rates may be integrated in time to produce estimates of total corrosion. Moreover, these estimates may be converted to equivalent material losses using the well-known Stern-Geary relationship if the anodic and cathodic Tafel or polarization constants  $\beta_a$  and  $\beta_c$  can be estimated. Although IJsseling quotes these values for his experiments, he suggests using an empirically obtained conversion.<sup>3</sup> This was used to obtain Figure 3, which shows our estimates of the corresponding total corrosion with time. It will be seen that in all cases the steady state corrosion condition is obtained very quickly (i.e., within 2 months), a feature which appears not to have been reported previously in field trials (since for these the first observation is often only at 3 months or 6 months). This is important because it indicates that the total amount of corrosion in the longer term is greatly influenced by the degree of corrosion that occurs soon after initial exposure.

Experimental observations of average corrosion rates obtained from weight loss measurements in pipeflow experiments are also of interest.<sup>4</sup> The experiments were carried out for durations varying between 36 days and 70 days at 10, 20, 30, 40, and  $50^\circ\text{C}$  and at 1.5 m/s velocity, using copper-nickel cylinders prepared with different surface conditions, some of little practical interest. In reporting the results, IJsseling, et al., averaged all the results and concluded that there was little difference among the average corrosion rates for 10, 20, and  $30^\circ\text{C}$  and that there was a substantially lower corrosion rate for specimens at  $40^\circ\text{C}$  and  $50^\circ\text{C}$ .<sup>4</sup> Although the latter is an important observation, more information can be extracted from the results.

Restricting attention only to the "as-delivered" specimens, the average corrosion rate can be plotted as a function of the total period of exposure (Figure 4). Data from Gudas and Hack,<sup>19</sup> Kato, et al.,<sup>20</sup> Lee,<sup>21</sup> and Ross<sup>22</sup> is shown also. Evidently, there is a high degree of nonlinearity of average corrosion rate with time. There is also a high degree of scatter in the data. Nevertheless, the overall trend of lower average corrosion rate with time is evident. Such a trend should be expected. However, there is a limit to this trend, as illustrated schematically in Figure 5. This figure shows that for a given steady corrosion curve,

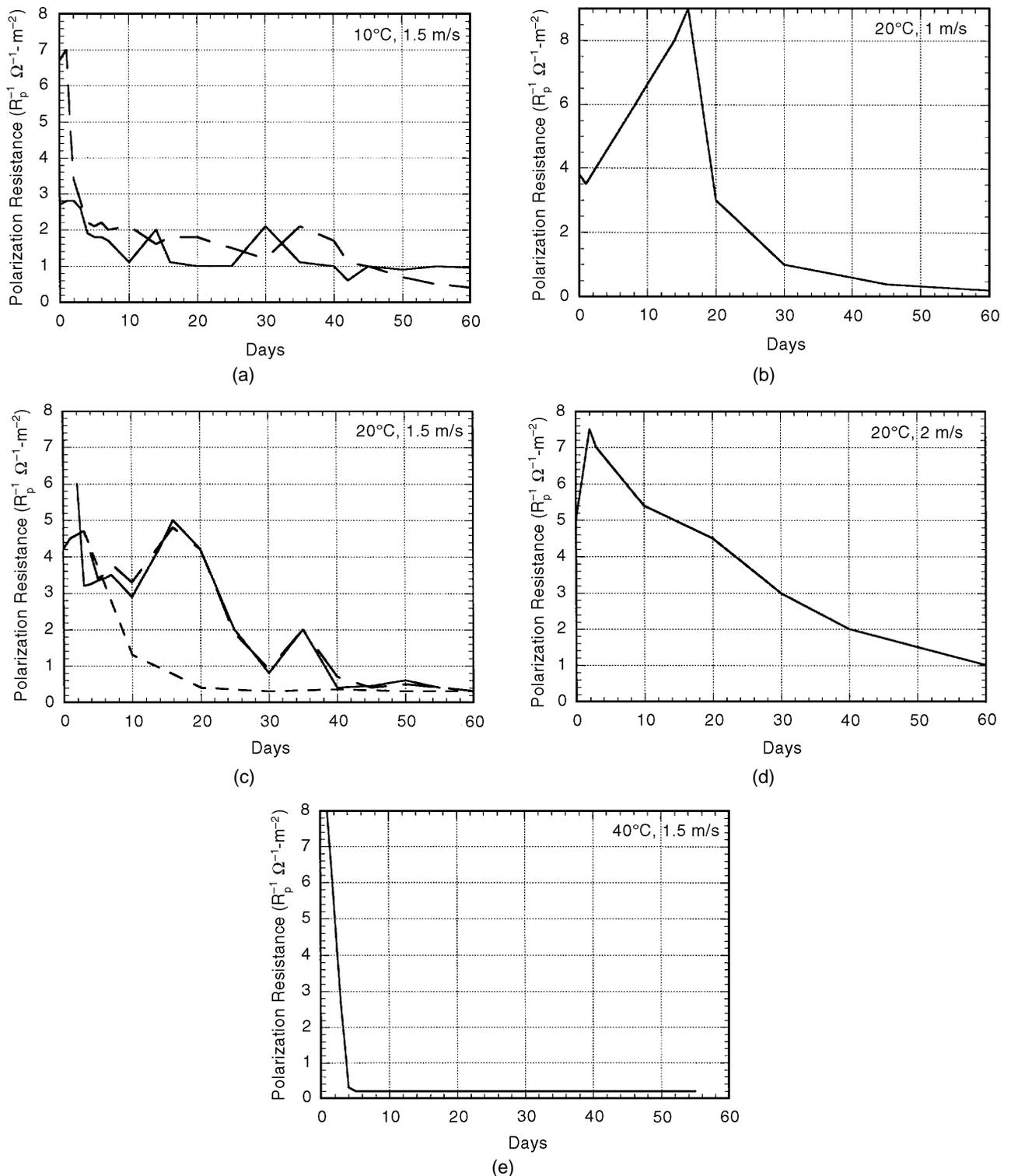


FIGURE 2. Typical polarization resistance measurements for short-term experiments (schematic).

as suggested by the previous observations for instantaneous corrosion rates  $\dot{c}$ , the average corrosion rate  $\bar{c}$  is always bounded by the  $c-t$  curve and will increase as time reduces, in a manner dictated by the longer term corrosion rate  $c_z$  and also the shape of the early part of the  $c-t$  curve. Moreover, since cor-

rosion cannot be negative, Bounding Case 1 (Figure 5[a]) presents the upper bound on the corrosion rate as it decreases with time. The actual corrosion rate must lie below this bound.

Following this line of argument indicates that a number of the average corrosion rates shown in Fig-

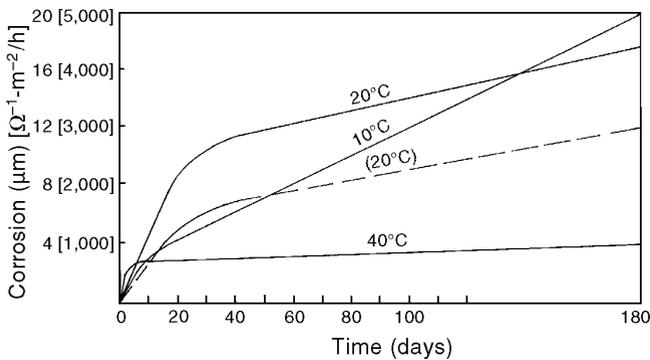


FIGURE 3. Total  $c-t$  estimates obtained from (numerical) integration of instantaneous corrosion rate-time plots shown in Figure 2.

ure 4 appear to be too high. One way this could occur is for the overall  $c-t$  curve to be greater, as suggested schematically in Figure 5(c). In turn, this suggests that the corresponding  $c-t$  curve for 20°C (and to a lesser extent that for 30°C) has a considerable degree of scatter (Figure 5[c]). This possibility is consistent with the rather large degree of scatter in experimentally obtained instantaneous corrosion rates (Figure 4).

The data in Figure 4 can also be viewed in a different way. For each of the IJsseling, et al.,<sup>4</sup> data sets (i.e., for each set of data for a given exposure period, see tables in Reference 4), Figure 6 shows average corrosion rate plotted as a function of water temperature. It is clear that for some data sets there is an apparently linear relationship, with average corrosion rate decreasing with increasing water temperature. For other data sets, however, no clear trends are evident even though the durations of all experiments and the experimental conditions were apparently

very similar. Clearly, any model attempting to deal with the influence of temperature on 90:10 copper-nickel corrosion must be able to account for this phenomenon. As will be seen, it is related to the scatter apparent in Figure 4.

## LONG-TERM TEMPERATURE EFFECT

In view of the observations about the short-term corrosion behavior of 90:10 copper-nickel, particularly the apparent stabilization of corrosion rate within ~ 2 months, it is considered appropriate to use the water temperature at the time of first immersion and for ~ 2 months thereafter as the critical parameter. For the ASTM worldwide data this is shown in Figure 7.

An estimate of the water temperature at first exposure was required for each site. This was based on the reported temperature range given in Appendix B used as the temperature extremes, the immersion date taken as the midpoint in the month unless better data is shown, and curves of temperature variation with time, such as shown in Figure 8. It was difficult to obtain complete information for all exposure sites. The temperatures at immersion shown in Appendix B are judged to be reasonable estimates, given the scatter in the water temperatures from year to year, as evident in Figure 8.

## DISCUSSION

In Figure 7, the region between 15°C and 27°C appears to be reasonably well-defined, but the lower temperature region depends entirely on the one set of results (DE). Other than some high velocity (9 m/s)

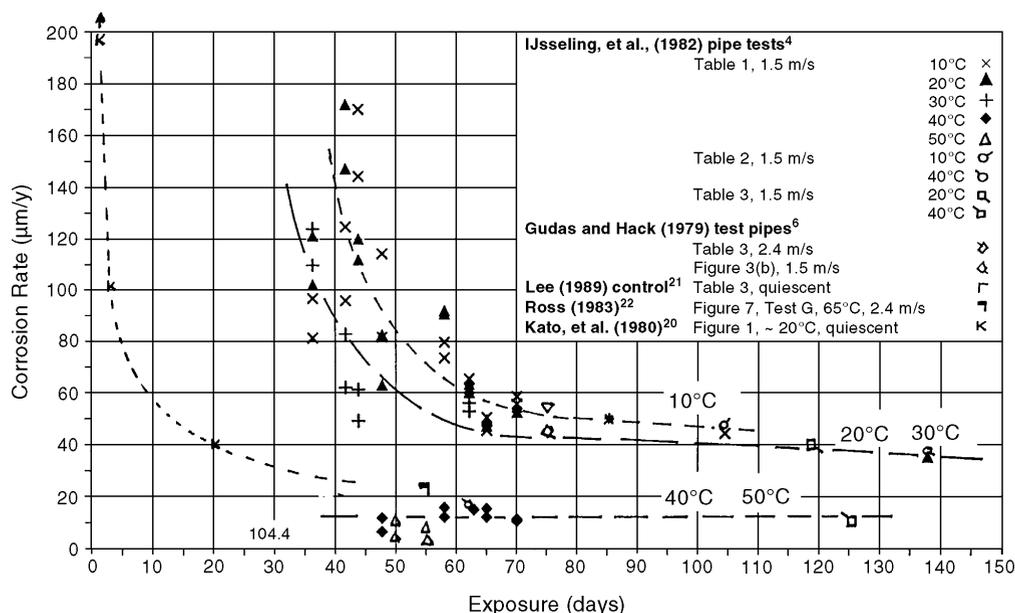
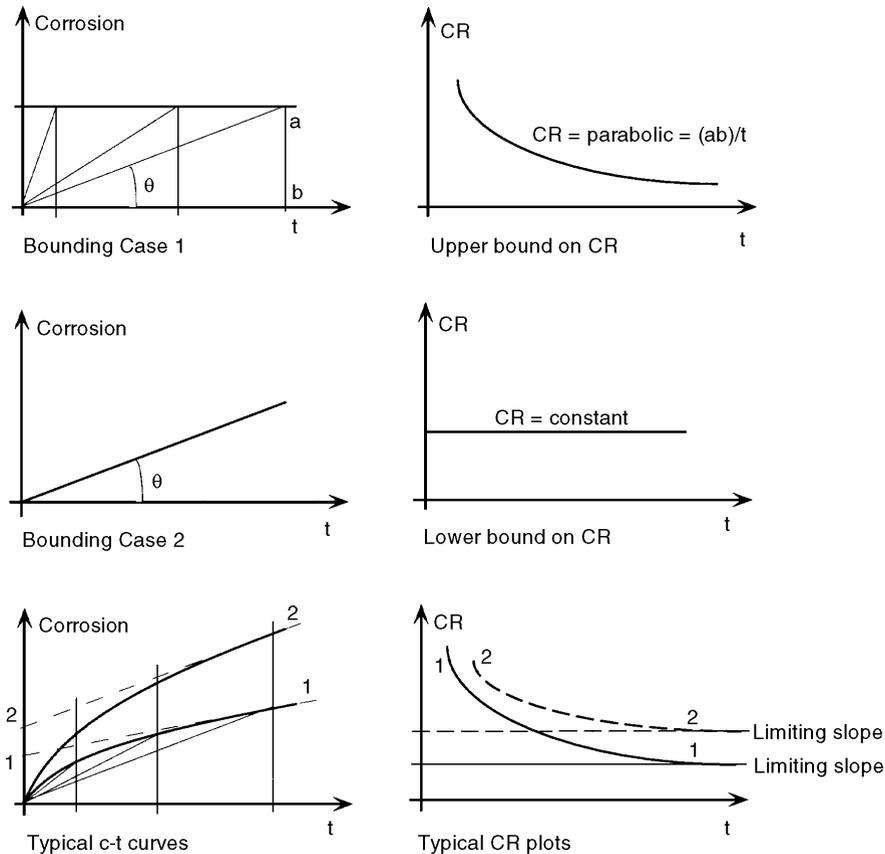


FIGURE 4. Average corrosion rate as a function of exposure time.



**FIGURE 5.** Schematic relationship between average corrosion rate (CR) and total corrosion as a function of exposure time ( $t$ ), showing upper limit on average corrosion rate (Case 1).

impingement weight loss data between 0°C and 15°C obtained by Mills and reviewed by Francis,<sup>23</sup> no other data appears to exist. That data suggests that corrosion decreases from ~ 5  $\mu\text{m}$  to 3.2  $\mu\text{m}$  between 0°C and 15°C, with most of this occurring between 10°C and 15°C. Since the exposure time was not defined, it is difficult to note other than that these observations are not inconsistent with those in Figure 7 and the expectation that corrosion should be negligible at water temperatures always < 0.

In an attempt to better define the higher-temperature region, a point is shown schematically at 40°C, based on extrapolation from the pipe corrosion measurements reported by IJsseling, et al.<sup>4</sup> A similar point could have been shown for 50°C. As noted above, corrosion at these temperatures was found to be very low despite water velocity being 1.5 m/s. It would be expected that in "at sea" conditions, with much lower water velocities, the corrosion would also be very low. Unfortunately, it has not been possible to relate to the present work the various reported laboratory results for higher-temperature corrosion of copper-nickel (e.g., Parvizi, et al.<sup>2</sup>) owing to unreported environmental conditions.

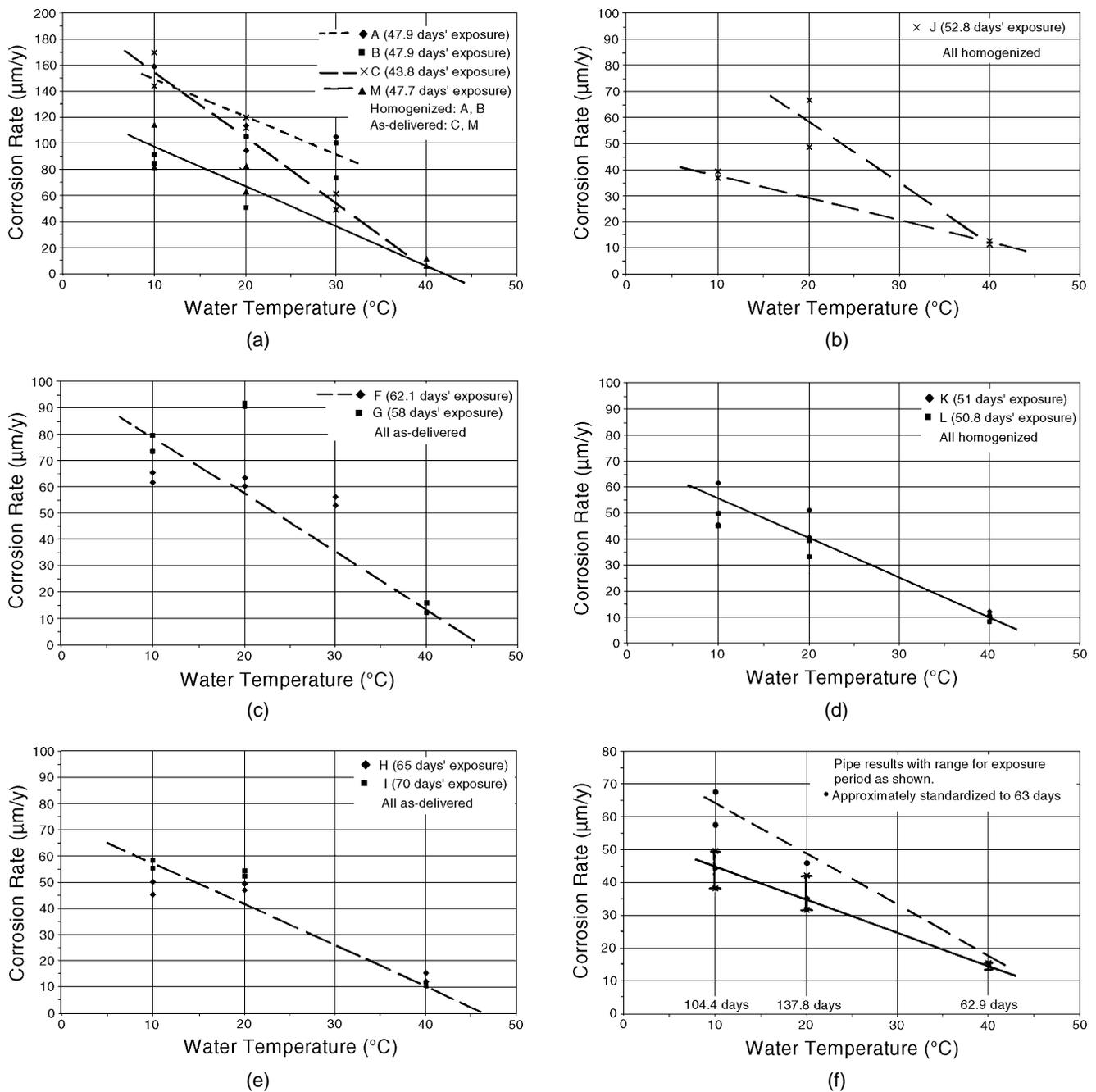
The data shown in Figure 7 for 0.5, 1, 3, and 5 year exposures are remarkably consistent, even

when it is recognized that the temperatures have been based on relatively unsophisticated data. Changing the estimates for temperatures at immersion does not have a significant effect on the shape of the curves (although they will change in detail). This lends confidence to the interpretation of the results.

Moreover, the  $c - t$  curves, while of unusual shape, are consistent with the effect of temperature observed by IJsseling and coworkers in their non-circulating pipeflow corrosion experiments.<sup>4-5</sup> This may be seen in Figure 7 when a line is drawn from the corrosion level at 10°C to that at 40°C for 5-year exposure. Such a line would cut through about the same curve at 20°C and at 30°C.

It is also clear from Figure 7 that relatively small variations in temperature in the range between 20°C and 30°C can give significantly different estimates of total corrosion. This observation is consistent with the sometimes large scatter in average corrosion rate observed in Figures 4 and 6.

For most sites a high degree of correlation appears to exist between the amount of corrosion recorded over the initial period and the subsequent corrosion rate. For this reason, the simplified approach of plotting all data as a function of initial immersion temperature has been adopted for Figure 7.



**FIGURE 6.** Corrosion as a function of seawater temperature for each data set in IJsseling, et al.,<sup>4</sup> and selected other data. (The data sets reported in Table I of Reference 4 are labeled A through M).

Further investigations will be required to untangle the effect of subsequent temperatures—the present data are insufficient to do this.

Some observations for other metals are of interest. For 70:30 copper-nickel, Wang, et al., noted that corrosion as determined from impedance measurements was lowest for the temperature range of  $\sim 40^{\circ}\text{C}$  to  $60^{\circ}\text{C}$ , with greater corrosion for higher and lower temperatures.<sup>24</sup>

For copper exposed to artificial seawater and various velocities to 0.3 m/s, a “dip” is evident at

$\sim 25^{\circ}\text{C}$  in the observations reported by Sawyer, et al.<sup>25</sup> A similar “dip” has been suggested for steel.<sup>9</sup> Observations on rotating flat copper and zinc specimens in artificial seawater by Mor and Beccaria revealed that the amount of corrosion of these metals decreased markedly from  $25^{\circ}\text{C}$  to  $40^{\circ}\text{C}$  and less so to  $60^{\circ}\text{C}$ .<sup>26</sup> Earlier, and without detailed reference, Tomashev noted very low corrosion ( $< 20 \text{ mg/dm}^2\text{-day}$ ) for zinc between  $20^{\circ}\text{C}$  and  $50^{\circ}\text{C}$ , at which point there was a sharp rise (to  $\sim 570$ ) followed by a gradual reduction ( $< 50$ ) at  $\sim 100^{\circ}\text{C}$ .<sup>27</sup>

Although there is clearly some conflicting evidence, these observations do suggest that very sharp changes in corrosion behavior, as noted in Figure 7 for 90:10 copper-nickel at  $\sim 20^{\circ}\text{C}$ , are not as unusual as might appear at first sight. Tomashev suggested that these sudden changes are attributable to changes in corrosion product,<sup>27</sup> a view shared by Wang, et al.<sup>24</sup>

Evidently, further investigations are required to firm-up the trends sketched above. This includes both the low-temperature region and the higher-temperature region. As noted, a number of observations exist for the high-temperature region but insufficient information has been reported in the literature to allow comparison to the present work. Also, the present work does not consider situations including artificial aeration.

Finally, it should be noted that, despite the considerable rise in corrosion rate at  $\sim 20^{\circ}\text{C}$  to  $25^{\circ}\text{C}$ , the overall corrosion of copper-nickel is remarkably low compared with most other metals for the whole temperature range considered herein.

## CONCLUSIONS

❖ Analysis of existing data for the immersion corrosion of 90:10 copper-nickel indicates that temperature at initial immersion of specimens can have a significant effect on observed long-term corrosion. The data also indicates that 90:10 copper-nickel exhibits a considerably higher level of longer-term corrosion as a result of immersion between  $\sim 18^{\circ}\text{C}$  and  $28^{\circ}\text{C}$  than at temperatures below and above this range. These observations, established mainly from an extensive ASTM corrosion study conducted during the 1980s over 14 sites worldwide, are consistent with the extensive laboratory studies of IJsseling and co-workers and with the limited field results previously reported by others for comparable corrosion conditions.

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A considerable number of people provided additional information about the site conditions for the ASTM study as shown in Appendix B (for details see Melchers<sup>9</sup>). Their efforts are acknowledged. For the present study, the author also acknowledges J. Ellor, Ocean City Research Center, New Jersey; A. Turnbull, National Physical Laboratories, U.K.; and J. Hill, DSTO-Innesfail, Australia for facilitating pro-

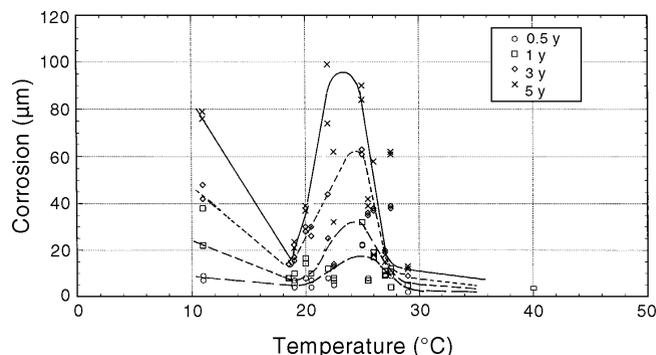


FIGURE 7. Variation of 90:10 CuNi corrosion as a function of initial immersion seawater temperature and exposure time.

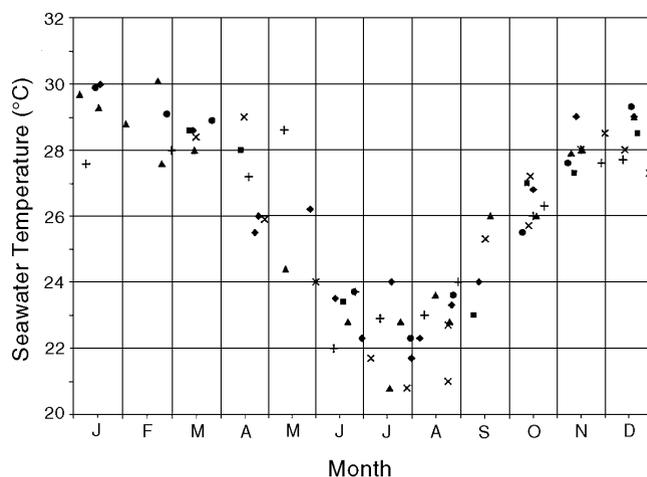


FIGURE 8. Observed seawater temperatures at 1-m depth at South Barnard Island, 1983-1992.

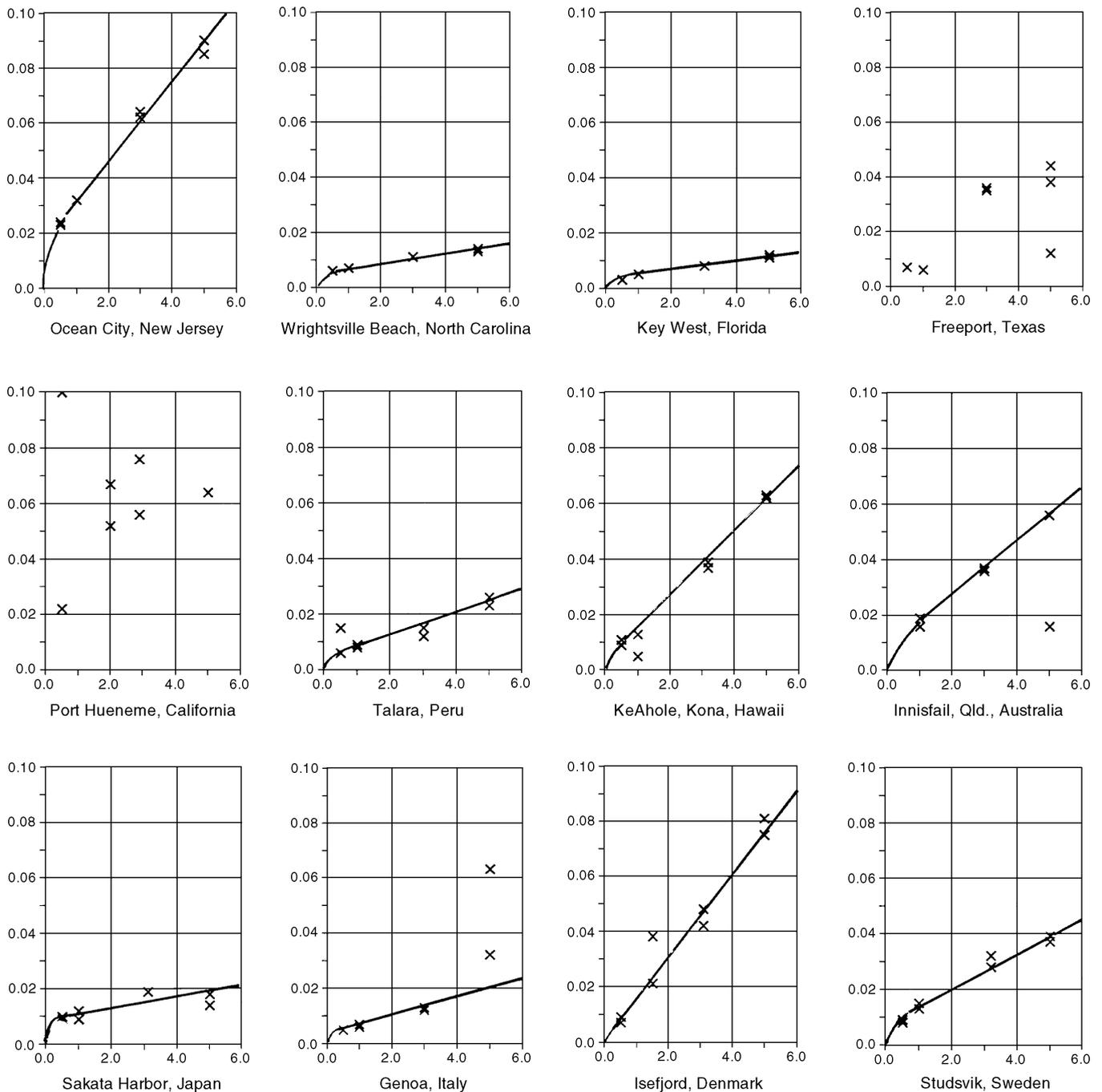
vision of long-term water temperature data for some typical corrosion sites.

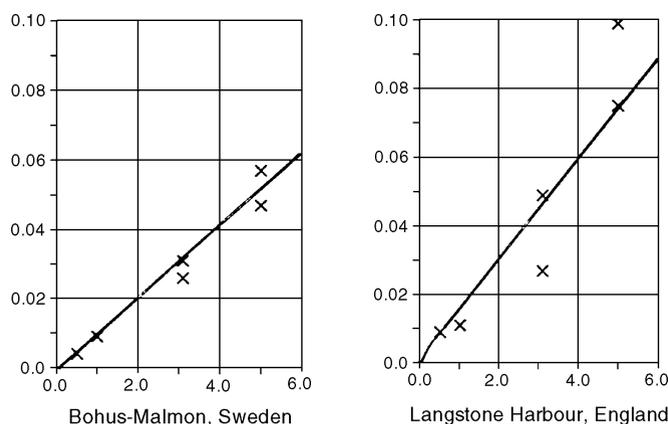
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## APPENDIX A—CORROSION LOSS (mm) vs EXPOSURE PERIOD (years)



APPENDIX B: DATA<sup>(A)</sup>

Key	Geographical Location	Test Site Description	Temperature Range (°C) (mean)	DO Range (change) (ppm)	Salinity	pH Range (change)	Initial Exposure Time	Initial Exposure Temperature (°C)
NJ	Ocean City, New Jersey	Inland waterway	1 to 29 (15)	5.2 to 11.7 (6.5) Not fully aerated	31 to 34	7.5 to 8.2 (0.7)	July 1983	25
NC	Wrightsville Beach, North Carolina	Timber pier north side of Banks Channel	7 to 30 (18.5)	5.0 to 9.6 (4.6) Not fully to fully aerated	31.8 to 37.6	7.9 to 8.2 (0.3)	May 1983	18.5
FL	Key West, Florida	Under pier at Fleming Key	16 to 31 (23.5)	4 to 8 (4) Not fully aerated	33 to 39	8.0 to 8.2	May 1983	29
TX	Freeport, Texas	Intake Flume	15 to 27 (21)	1.5 to 6.0 (4.5) Not fully aerated	21.1 to 35.3	7.5 to 8.6 (0.9)	October 1983	25
CA	Port Hueneme Harbour, California	Harbor mouth exposed to sea	14 to 21 (17.5)	3.6 to 5.3 (1.7) Fully aerated	33	7.9 to 8.1	May 1983	17.5
PE	Talara, Peru	180 m from shore, on pier	18 to 22 (20)	5 to 6 (1.0) Fully aerated	35.8	8.2	March 1984	19
HI	Keahole, Hawaii	45 m from shore, on pipe at unknown depth	24 to 28 (26)	6 to 14 (8.0) Fully aerated	34.6 to 35	8.0 to 8.3 (0.3)	July 1983	27.5
AU	North Barnard Island, Australia	Raft well offshore unpopulated region	21 to 30 (25.5)	5.1 to 6.5 (1.4) Fully aerated	31.7 to 37.2	8.2 to 8.3	July 1986 (mid-winter)	26 (actual)
JA	Sakata Harbour, Japan	From docking pier close to shore	2 to 28 (15)	7.1 to 13 (5.9) Low	30.6 to 33.3	8.4	August 1983	27.5
IT	Genoa Harbour, Italy	Raft in inner harbour, near shipping, city	11 to 25 (18)	5.8 to 8.9 (3.1) Not fully aerated	38.2 to 36.6	8.1 to 8.3	September 1983	22.5
DE	Isefjord, Denmark	Raft in fjord, no other details	0 to 18 (9)	NA—not fully aerated?	18 to 28	7.5 to 8.0 (0.5)	October 1983	11
ST	Studsvik, Sweden	From wooden bulkhead; no details	2 to 20 (11)	6 to 10 (4.0) Not fully aerated?	7.8 to 8.1	7.4 to 7.6	August 1983	20
BM	Bohus-Malmon, Sweden	From raft; no other details	2 to 20 (11)	6 to 10 (4.0) Not fully aerated?	21 to 28	8.0 to 8.2	August 1983	20
EN	Langstone Harbour, U.K.	From raft moored at center of water body	5 to 22 (13.5)	8.8 to 11.8 (3.0) On avg fully aerated	34 to 34.6	8.0 to 8.2	August 1983	22

<sup>(A)</sup> Adapted, with permission, from STP 1300-Corrosion Testing in Natural Waters, Volume 2, copyright American Society for Testing and Materials, 100 Barr Harbor Drive, West Conshohocken, PA 19428.

Note: Data from Phull, et al., as amended using more detailed information obtained from correspondents.<sup>8</sup>