

# Environmental influences on the vapourside corrosion of copper-nickel alloys

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## Abstract

This paper describes an experimental study of the detailed influences of three major environmental parameters, temperature, carbon dioxide and oxygen, on the vapourside corrosion of Cu/Ni. The Cu/Ni materials in the investigation contained between 10 and 64% nickel but with emphasis on Cu/10Ni-base and Cu/30Ni-base alloys which are widely employed for heat-transfer tubes. Electrochemical techniques were used to investigate the corrosion behaviour of these alloys in distilled water at temperatures of 20–90°C with, and without, the injection of carbon dioxide and oxygen. In the less-aggressive conditions of low temperature and pH=6, there was a general trend of improved corrosion resistance with increasing nickel content of the alloy but the distinctions between the Cu/10Ni and Cu/30Ni alloys were observed to decrease in more aggressive conditions (such as higher temperatures and in the presence of dissolved carbon dioxide). The work confirmed that the combined presence of dissolved carbon dioxide and oxygen represents a relatively aggressive environment for copper-nickel alloys but it was also demonstrated that carbon dioxide in conjunction with extremely low oxygen concentrations can exert a significant deleterious influence on the corrosion behaviour of these alloys.

*Keywords:* Copper-nickel; Corrosion; Pure water; Carbon dioxide

## 1. Introduction

Partly on account of their generally good durability, especially in terms of waterside performance, copper/nickel alloys are the most widely

used heat transfer tubes in modern thermal desalination plants. However, there have been a number of cases [1–5] of corrosion problems comprising attack of these alloys on the tube vapourside in the high temperature stages of multistage flash desalination and multi-effect

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distillers. The failures are located in the high-temperature stages but not necessarily in the top-temperature ones. The tube failures are occurring after quite a number of years of operation but after operational periods much shorter than projected plant lifetimes. The operational problem is clearly critically dependent upon the actual chemical and physical environment to which the tubes are exposed in the condensing vapour and this is extremely complex and indeed difficult to measure and hence to characterise. One aggressive agent, which (in units employing scale-control inhibitors) will inevitably be present in the vapour space, is carbon dioxide that yields acidic conditions in the condensing water film. There is also the likelihood of the presence of oxygen either as a result of incomplete deaeration of the feed or from in-leakage and, in some cases, the vapour may include chlorine, hydrogen sulphide and ammonia.

Whichever of the above-mentioned non-condensable gases are implicated, a critical aspect in plants is the venting system and the main effort in counteracting vapourside corrosion (VSC) in affected plants has been towards modification of the venting system.

It is clearly advisable for the engineering strategies to be supplemented by studies aimed at obtaining basic understanding of the mechanisms of the VSC processes and a small number of such investigations [6–9] have been focused on this issue. The rationale for such studies is to undertake experiments in controlled conditions that permit

reasonably unambiguous interpretation without the complexities associated with findings linked to long-term operation of plant in possibly-varying conditions. Previous work [6,8] examined the corrosion behaviour of relevant copper/nickel alloys containing 10%Ni and 30%Ni and investigated the influence of temperature and the presence of dissolved CO<sub>2</sub>. These studies [6,8] demonstrated complexities associated with the influence of the alloy nickel content and the effect of the presence of carbon dioxide. Postulations, on the role of oxygen in the VSC process, have also been made by others [7]. The present investigation was undertaken to shed more light on the important issue of the influence of carbon dioxide and oxygen. The study also included a higher nickel alloy, Monel 400, in order to provide more understanding of the role of nickel in the practically-used, lower-nickel materials.

## 2. Experimental

The corrosion behaviour of a range of copper/nickel alloys was studied:-

- copper-10%nickel alloy: obtained from two sources and hereinafter designated, Cu-10Ni/1 and Cu-10Ni/2 respectively
- copper-30% nickel alloy, hereinafter designated, Cu-30Ni
- the high iron-and high-manganese version of the copper-30% nickel alloy, hereinafter designated, Cu-30Ni/M

Table 1  
Composition of copper/nickel alloys studied, %

Material	Cu	Ni	Fe	Mn
Cu-10Ni/1: BS2874 CN102 (25 mm diameter bar)	86.5	10.6	1.7	0.7
Cu-10Ni/2: BS2871 CN102 (2.5 mm thick plate)	85.6	11.4	1.9	0.7
Cu-30Ni: NES780 ISS.2 (25 mm diameter bar)	67.9	30.6	0.7	0.7
Cu-30Ni/M UNS C 71640 (tube, 25 mm ext. diameter)	65.5	29.1	2.2	2.0
Monel 400: UNS N 04400 (12.7 mm diameter bar)	32.8	64.2	1.7	0.9

- the high-nickel alloy, Monel 400.

The detailed compositions are given in Table 1.

The plate material was cut into specimens of 1 cm × 1 cm. From the bar materials, specimens of height 10 mm were cut. Cross-section rings were sliced from the tube material.

To facilitate electrochemical monitoring, an electrical connecting wire was attached to the back face of specimens after which they were encapsulated in a temperature resistant resin. Finally, the exposed faces of the specimens were ground through a series of silicon carbide papers to a 800 grit finish before washing and degreasing.

The test specimens were immersed, at controlled temperatures of  $20 \pm 1^\circ\text{C}$ – $80 \pm 2^\circ\text{C}$ , in the following environments :-

- distilled water, of  $1.5\text{--}7 \mu\text{S}/\text{cm}$  ( $25^\circ\text{C}$ ) conductivity, in a flask open to the normal air atmosphere
- distilled water in an enclosed glass vessel into which carbon dioxide and other gases could be bubbled
- distilled water acidified, using hydrochloric acid, to controlled pH values of 3.0, 4.0, 5.0 in a flask open to the normal air atmosphere.

The corrosion processes were followed by electrochemical monitoring which involved DC potentiodynamic sweeps utilising a computer controlled potentiostat/scan generator with a three-electrode cell. In order to obtain meaningful reproducible results in the low-conductivity water, the three-electrode system was of the form shown in Fig. 1 in which the counter electrode was a piece of titanium enclosed in epoxy resin. The specimen-to counter electrode distance was maintained at 2.5 mm and the electrode potentials were measured using an Ag/AgCl reference electrode and a salt bridge whose small-diameter (1.5 mm) tip was located close to the specimen as shown in Fig. 1. The polarisation

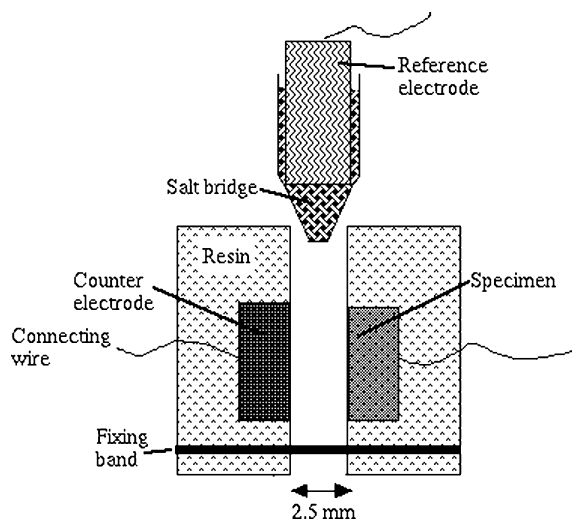


Fig. 1. Schematic representation of the specimen set-up (not to scale).

scans comprised scanning the specimen electrode potential at 15 mV/min. in either the positive (anodic) or negative (cathodic) direction from the natural, free-corrosion potential,  $E_{\text{corr}}$ .

Two types of potentiodynamic sweep were undertaken:-

sweeps over a potential range of several hundred mV

anodic scans over a small potential range of 20–40 mV.

The longer scans provide a more detailed indication of the polarisation behaviour but can only reliably be carried out once on any particular specimen. The shorter sweeps can be undertaken many times on a single specimen and yield a value of the polarisation resistance,  $R_p$  from the gradients of the linear potential current plots [10].  $R_p$  values quoted in this paper are in units of  $\text{kohm cm}^2$ .

### 3. Results

#### 3.1. Comparison of alloys

Figure 2 shows the results of anodic polarisation scans on three of the alloys after 1 h

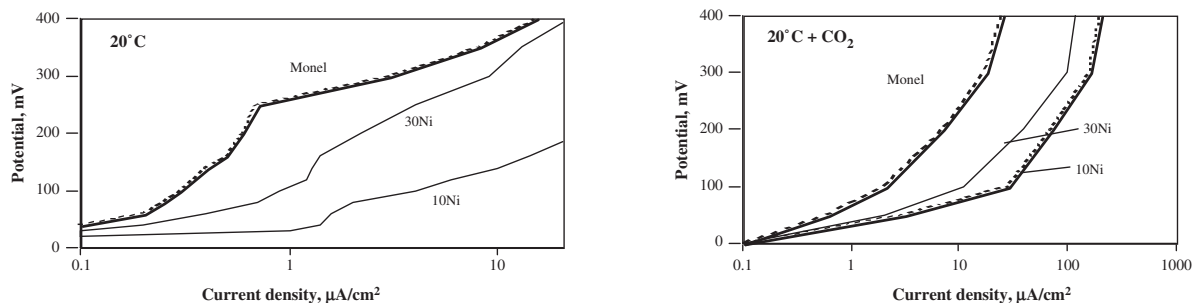


Fig. 2. Anodic polarisation curves, at 20°C, of Cu-10Ni/1 and Cu-30Ni after 1 h in distilled water open to air (left) and with CO<sub>2</sub> injection in enclosed vessel (right).

in distilled water at 20°C. (To facilitate comparisons, the  $E_{\text{CORR}}$  values for the three alloys have been set as zero.) With the water open to air (pH about 6) the lower rates of current increase as the potential is shifted from  $E_{\text{CORR}}$  demonstrate the beneficial influence of higher alloy nickel contents. The injection of CO<sub>2</sub> increases the rates of corrosion (as shown by the faster rates of current increase with potential) but significantly reduces the differentials in performance of the three alloys. The similarities in the polarisation behaviour, of the 10Ni and 30%Ni alloys in the more aggressive conditions of CO<sub>2</sub> injection at 70°C, are further displayed in Fig. 3.

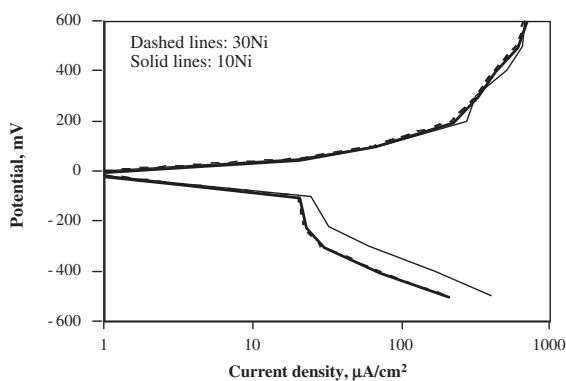


Fig. 3. Anodic and cathodic polarisation curves, of Cu-10Ni/1 and Cu-30Ni at 70°C, with CO<sub>2</sub> injection in enclosed vessel.

Fig. 4 displays some distinctions between the 10Ni and 30Ni alloys in respect of their response to changes in the environment. Although, as expected the corrosion rate of both alloys increases with temperature and the presence of CO<sub>2</sub>, the sensitivity of the 10Ni material is greater in respect of temperature whereas the 30Ni alloy becomes especially vulnerable to increased attack when CO<sub>2</sub> is present.

### 3.2. Effect of dosing with hydrochloric acid

In order to examine the basic effect of pH on the corrosion of copper-nickel alloys, experiments were carried out in which the acid conditions were induced by dosing with hydrochloric acid. These experiments were conducted in vessels open to atmospheric air (i.e. in relatively high-oxygen conditions) and the results are summarised in Fig. 5 and Table 2. The effect of pH on the anodic polarisation behaviour at 20°C of the Cu-30Ni/M alloy is shown in Fig. 5. There is a gradual progression of more active behaviour between pH=6 (un-dosed distilled water) and pH=4 and a relatively large jump in reaction rate at the lowest pH of 3. The equivalent experiments on the Cu-10Ni/2 material showed a more gradual progression to more active behaviour between pH 6 and 4 but with a similar large shift between pH 4 and

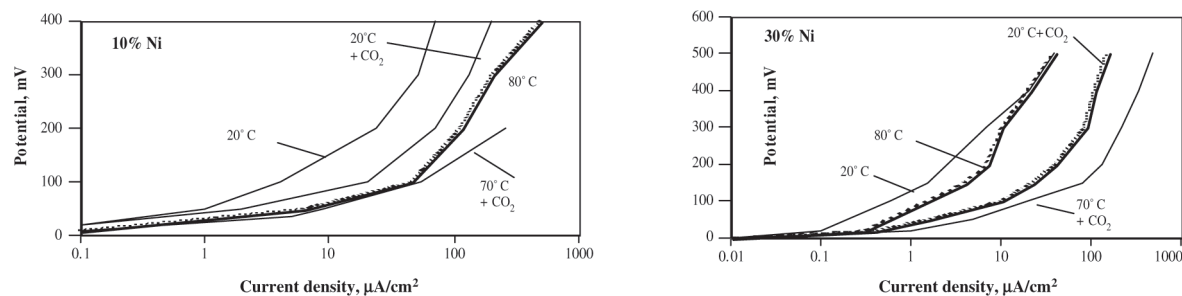


Fig. 4. Effect of conditions on anodic polarisation curves, of Cu-10Ni/1 and Cu-30Ni.

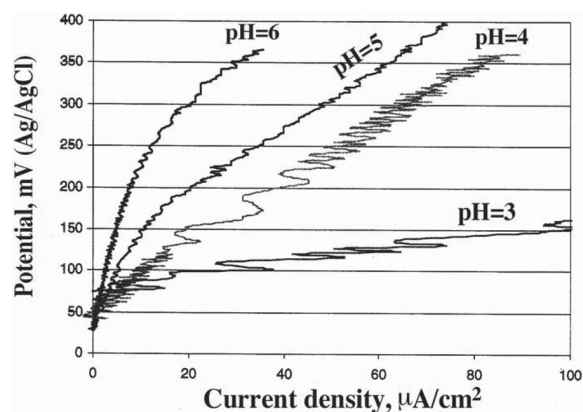


Fig. 5. Effect of pH on anodic polarisation of Cu-30Ni/M at 20°C.

3. These effects of pH on corrosion behaviour are also demonstrated in Table 2 in which the polarisation resistance ( $R_p$ ) values obtained at 20°C and 70°C are presented. The values of  $R_p$  in Table 2 were obtained from the gradients of potential/current plots in the region 20 mV more positive to  $E_{corr}$ . The data in Table 2 displays reductions in  $R_p$  Table 2

Effect of pH on polarisation resistance ( $R_p$ )

pH	Cu-10Ni/2		Cu-30Ni/M	
	$R_p$ (20°C)	$R_p$ (70°C)	$R_p$ (20°C)	$R_p$ (70°C)
6	16.1	8.0	35.4	8.4
5	9.0		17.4	
4	4.4	1.3	5.8	0.61
3	0.56	0.4	1.3	0.49

which is inversely proportional to the corrosion rate [10]. The relatively large increase in corrosion rate between pH 4 and 3 is particularly evident for the 10%Ni alloy at 20°C

### 3.3. Experiments involving injection of different gases

These experiments comprised undertaking the short polarisation scans during consecutive periods of gas injection to an enclosed vessel in a single test, i.e. without any other disturbance of the specimen. An important feature of these experiments was the extremely low oxygen contents in the distilled water consequent upon the gas injection into an otherwise sealed vessel. Measurements, using a colourimetric dissolved oxygen test kit, demonstrated a dissolved oxygen concentration of < 50 ppb in the sealed vessel during injection of CO<sub>2</sub>. The resulting values of polarisation resistance,  $R_p$ , for tests at 70°C are shown in Table 3. These results reveal, for both 10Ni and 30Ni alloys, a large decrease in  $R_p$  (i.e. proportionate increase in corrosion rate) occurring upon injection of CO<sub>2</sub>. For the 10Ni alloy, there was a further increase in corrosion rate with the additional injection of air.

In a second series of tests on the Cu-10Ni/2 alloy, the above trends were replicated and, additionally, a reduction in rate was observed

(Table 4) when the temperature was raised between 80°C and 90°C and a reversal upon cooling back to 80°C. These temperature effects were coincident with changes in pH between 4.8 (70°C) and 5.1 (90°C).

Figure 6 shows the same effect (sharp increase in the rate), upon injection of CO<sub>2</sub>, on the anodic polarisation behaviour of the (lower Fe/Mn) Cu-30Ni alloy. Even after stopping the CO<sub>2</sub> supply, the anodic reaction rates remained higher than before CO<sub>2</sub> addition – although they do display the expected decline as the content of the CO<sub>2</sub> in the water decreased.

#### 4. Discussion

The results demonstrate the beneficial effect of higher nickel content of the alloy in the mild acidic conditions encountered in distilled water (pH=6). This is in line with earlier findings [6,8] and also with the general view of the role of nickel in promoting increased corrosion resistance due to the formation of a more protective corrosion product film [11–13]. This less protective film on Cu-10Ni, in the mild acidic conditions

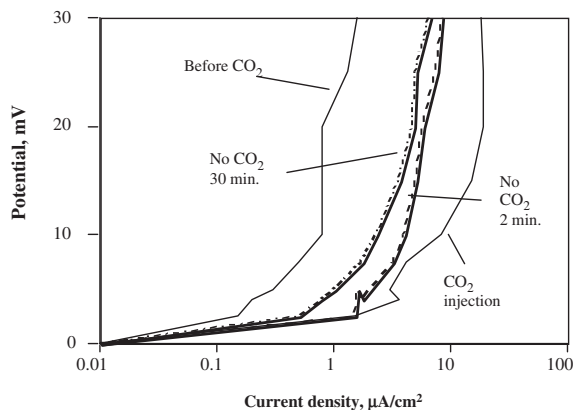


Fig. 6. Effect of CO<sub>2</sub> injection on anodic polarisation of Cu-30Ni: dashed and dotted curves show behaviour 2 min and 30 min. after switching off the CO<sub>2</sub> supply.

represented by distilled water, is reflected in a significant reduction in corrosion resistance accompanying an increase in temperature between 20°C and 80°C. Such a rise in temperature does not have such a deleterious effect on the 30%nickel alloys.

Decreases in pH are considered [11,13] to reduce the corrosion resistance of even the higher-nickel alloys and this is demonstrated in the results (Fig. 5, Table 2) of the present study. The large jump in corrosion rate consequent upon a pH change between 4 and 3 at 20°C (Fig. 5, Table 2) is in agreement with other work on Cu-50%Ni [11] in which study this effect was shown to be associated with more copper dissolution in conditions of poor passivity.

In fact, the present study has shown that the differentials in corrosion behaviour between the 10Ni and 30Ni copper-nickel alloys are considerably reduced when CO<sub>2</sub> is injected into the distilled water – forcing the pH down to < 5. This convergence of the corrosion behaviour of copper-nickel alloys containing 10% and 30% nickel in the presence of CO<sub>2</sub> has been observed earlier [6,8] but detailed assessments of the influence of CO<sub>2</sub> in this previous work [8] were hindered somewhat by scatter in the observations from different experiments on separate specimens. This uncertainty has been overcome in the present study in which changes in polarisation response of single (otherwise uninterrupted) specimens, when subject to the injection of different gases (Tables 3 and 4, Fig. 6). have facilitated unambiguous assessment of the deleterious effect of the presence of CO<sub>2</sub>.

Thus the effect of the presence of CO<sub>2</sub> is, via the concomitant decrease in pH, to destabilise the protective surface film that affords good protection to a 30%Ni alloy in distilled water. In this respect, it was shown previously [6] that injection of CO<sub>2</sub> rapidly caused an increase in corrosion rate of

Table 3  
Effect of injection of different gases at 70°C on polarisation resistance ( $R_p$ )

Injected gas	$R_p$ Cu-10Ni/2	$R_p$ Cu-30Ni/M
N <sub>2</sub> (pH=5.7)	10.5	9.9
N <sub>2</sub> +CO <sub>2</sub> (pH=4.9)	6.9	3.9
CO <sub>2</sub> (pH=4.7)	5.7	3.9
CO <sub>2</sub> +air	1.3	3.7, 3.9*

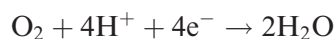
\*replicate test

Table 4  
Effect of temperature on polarisation resistance of Cu-10Ni/2

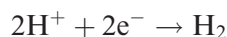
Injected gas	Temperature, °C	$R_p$ Cu-10Ni
CO <sub>2</sub>	70	6.3
CO <sub>2</sub> +air (pH=4.8)	70	4.5
CO <sub>2</sub> +air (pH=5.1)	90	6.2
CO <sub>2</sub> +air	70	3.7

copper-nickel alloy specimens that had been subject to prior 70–87-day periods of exposure to the less-aggressive conditions of distilled water at 20°C without CO<sub>2</sub> injection. This indicated that even a relatively short excursion into high-CO<sub>2</sub> conditions can damage a mature protective film obtained in less-aggressive distilled water.

It is evident that this absence of a protective film in the presence of the acidic gas, CO<sub>2</sub>, facilitates a relatively rapid corrosion rate of copper-nickel alloys involving the oxygen-reduction cathodic reaction:-



It should be pointed out that the measured values of  $E_{\text{corr}}$  at the beginning of the various experiments in this study were all around zero volts Ag/AgCl, i.e. several hundred mV more positive than the equilibrium electrode potential,  $E_0^{\circ}$ , for the hydrogen evolution reaction:-



at any of the pH values encountered in this investigation.

Thus, in none of the experimental conditions of this study could hydrogen evolution represent the cathodic reaction under free corrosion conditions. This comparison of electrode potentials confirms the role of oxygen in the acidic corrosion of copper-nickel alloys. Of some definite practical significance, however, has been the demonstration that such relatively rapid corrosion can occur at extremely low oxygen concentrations of much less than 50 ppb. These levels of oxygen are approaching what could be realistically expected during desalination plant operation even with efficient de-oxygenation of the seawater feed and negligible air in-leakage. In other words, the presence of CO<sub>2</sub> gas pockets in the vapour space is certain to promote significantly enhanced corrosion rates of copper-nickel alloys in all practically obtainable conditions in thermal desalination plant. Moreover, there is clearly no significant benefit secured by employing a copper-30% nickel alloy (either the basic alloy or higher Fe/Mn versions).

The experiments (Table 4), involving temperature changes between 70 and 90°C in the presence of CO<sub>2</sub>, were associated with slight increases of pH as the temperature was raised between 70°C and 90°C – possibly due to lower gas solubility at the higher temperature.

## 5. Conclusions

Higher nickel contents in copper-nickel alloys confer increased corrosion resistance in distilled water at 20°C.

However, the differentials in corrosion behaviour between copper-nickel alloys of different nickel content are substantially reduced in more aggressive conditions associated with the presence of CO<sub>2</sub> especially at elevated temperatures (70°C). There appears to be no significant benefit accruing from the

use of 30%Ni alloys (rather than material with 10%Ni) in the aggressive conditions.

The deleterious influence of CO<sub>2</sub> is due to the resulting acidic conditions causing de-stabilisation of the protective corrosion product films.

The corrosion process in the acid conditions occurs even in the presence of extremely low dissolved oxygen concentrations typical of desalination plant incorporating very efficient oxygen-elimination procedures.

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