

Evaluation of Copper-Nickel as a Sheathing Material for Hot Riser Protection on Offshore Platforms

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Summary

C70600 and C71500 copper-nickel alloys have been used for sea water systems on offshore platforms as well as commercial and naval ships for many years. They have also been used as condensers and heat exchangers in a variety of industries. The C70600 alloy has also been evaluated for splash zone protection sheathing on pilings and has over 20 years excellent service on the legs of Phase 1 of the Morecambe Field platforms. More recently there has been interest in the use of copper-nickel as a splash zone sheathing for import and export risers where metal temperature may be as high as 110°C. Although experience from other applications would indicate that these alloys would be most suitable, there is a lack of data to assess the behaviour of the alloys in oxygenated sea water at high temperature and tests were needed to assess this with more confidence. Nickel-copper alloy 400 has a long track record as a hot riser sheathing material on offshore platforms and this was included in the trials as a comparison.

Test work has been carried out using substitute sea water at 100°C with oxygen bubbled through the solution. The test was performed in reflux condensers for 1000 hours and evaluations were carried out to assess the corrosion behaviour of the C70600 copper-nickel in terms of general weight loss corrosion, crevice corrosion and pitting. The C71500 alloy and alloy 400 were assessed visually for localised corrosion only.

The results revealed that C70600 and C71500 copper-nickels have better resistance to pitting and crevice corrosion than alloy 400 under these conditions. This indicated that either alloy would potentially offer a suitable and more economic, alternative as a hot riser sheathing material.

Keywords: copper alloy, alloy 400, hot splash-zone sheathing, offshore structure, corrosion test, seawater corrosion

Introduction

Copper-nickel alloys C70600 and C71500 have 10% and 30% nickel respectively; they have a long track record for sea water service in naval and commercial shipping, desalination and offshore systems. In the 1980s, the 90-10 alloy was chosen for splash zone sheathing for legs of the platforms in Phase 1 of the Morecambe gas field and, over 20 years on, this has shown excellent service. At the same time as Morecambe Field development began, the International Copper Association initiated an experimental programme at the LaQue Center for Corrosion Technology in North Carolina to examine the behaviour of copper-nickel in closer detail in terms of corrosion resistance and biofouling on sheathed pilings. The results of this work [1], summarised later, have added to the overall understanding of the alloy's capabilities.

65% nickel-copper, alloy 400 (N04400) metal sheathing has normally been used for splash zone protection in the more taxing application of hot risers and has given good service. However, with current metal prices at very high levels, it was queried for a North Sea project whether copper-nickels would be a valid and more economic material for sheathing hot risers given the much lower nickel content (10 or 30% compared to 65%). The metal temperature for the risers in this case could achieve 110°C and they would be exposed to splash and spray and immersion by cold aerated sea water.

The copper-nickel alloys are standard marine condenser and heat exchanger materials and, as such, used at elevated temperatures in contact with sea water. In terms of localised corrosion, they do not suffer from chloride stress corrosion or have a crevice corrosion or pitting limitation in chloride environments as stainless steels do. Copper-nickel is often recommended for temperatures up to around 75°C in aerated water [2] but there is less information for 75-110°C. They are used for Multistage Stage Flash (MSF) Desalination where temperatures can be high in the brine heater (~120°C) and hotter areas of the Heat Recovery sections. However, although there is much experience in MSF plants, the brine is de-aerated which is less aggressive than the aerated seawater in contact with risers.

To provide more confidence that 90-10 copper-nickel would be a satisfactory replacement for alloy 400 (N04400), it was necessary to review the available literature and to initiate trials comparing the corrosion resistance of hot surfaces of alloy 400 with 90-10 and 70-30 copper-nickels in contact with aerated sea water.

Literature Overview

The Metal Sheathing Concept.

Corrosion of an unprotected steel structure in seawater varies with position relative to the mean high and low tide level as shown in Figure 1.

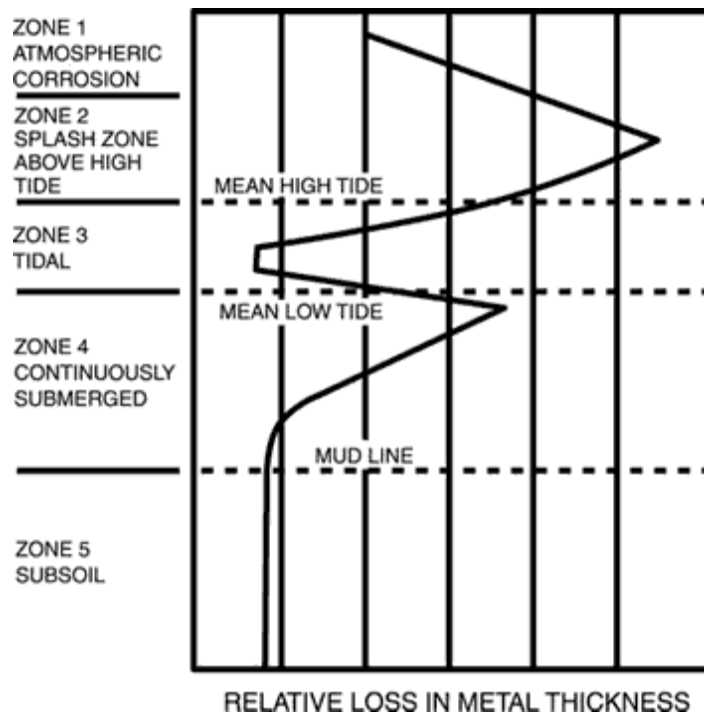


Figure 1. Profile of the Thickness Loss Resulting from Corrosion of an Unprotected Steel Structure in Seawater [2]

The spray and splash zone above the mean high tide level is the most severely attacked region due to continuous contact with highly aerated sea water and the erosive effects of spray, waves and tidal actions. Corrosion rates as high as 0.9 mm/a at Cook Inlet, Alaska, and 1.4 mm/a in the Gulf of Mexico have been reported[3] and values at least as high could be expected in the North Sea. Cathodic protection in this area is ineffective because of lack of continuous contact with the seawater and current does not flow for much of the time. Therefore some form of protective coating is required in this area.

Corrosion rates of bare steel pilings are often also high at a position just below the tidal zone at the top of the submerged zone. This is generally considered to be the result of galvanic action between the steel in the highly aerated tidal zone acting as a cathode and steel in the relatively air-depleted submerged zone corroding as the anode. Attack in this area may also be affected by sand, waves and fast tidal flow depending particularly in shallower waters. Corrosion of this submerged zone can be suppressed by cathodic protection.

Metal sheathing has proved to be a very successful method of protection when applied in the region through the splash/spray zone to just below the tidal zone. As early as 1949, 65% nickel-copper (Alloy 400) was used on an offshore platform in the Gulf of Mexico [3, 4]. Steel legs of a drilling platform were sheathed with 1.27mm sheet. After 26 years, no significant corrosion was reported [3]. Experience elsewhere in the intervening years has been very good and wide scale use has been reported in the Middle East, North Sea, South East Asia and USA [4,5].

Early Trials

The LaQue Center for Corrosion Technology at Wrightsville Beach, North Carolina, USA, conducted extensive trials of sheathing using the steel piling which support the sea water corrosion test wharves at the laboratory as test specimens. Sea water temperatures vary seasonally between 6-29°C. Sheathing materials tested included 65% nickel-copper (Alloy 400) sheet, 70-30 copper-nickel sheet and 65% nickel-copper (Alloy 400) clad steel. All of these were reported to be performing very well after 39 years of exposure [4]. A large number of proprietary coatings, including galvanizing and sprayed zinc and aluminium, were also tested; all proved to have finite effective lifetimes extending up to 13 years [6]. 90-10 copper-nickel was not included in these early sheathing trials as the alloy was still being developed at that time.

In the early trials, the 65% nickel-copper alloy and the 70-30 copper-nickel alloy sheaths were welded directly to the steel. A number of experiments examined corrosion of the anodic steel below the tidal zone as it would normally be anticipated that corrosion in that area would be accelerated due to direct contact with the nobler sheathing alloy [3]. In practice, steel below the tidal zone was found to corrode less when in contact with the sheathing than if the steel in that area was left unsheathed. The effect was attributed to the precipitation of calcareous deposit on the cathodic sheathing metal which forms an insulating barrier that reduces cathodic reactions. The corrosion product on the bare steel in the tidal zone is unable to maintain such protective scale and accounts for the greater galvanic effect on the submerged steel.

This conclusion was confirmed by the results of galvanic corrosion tests conducted to determine the effects on submerged steel coupled to other alloys in the zone between high and low tides [3, 6] as shown in Figure 2. Plates of the alloys placed in the tidal zone were coupled to submerged steel plates, and the total current per tide was measured periodically over the 14-months of exposure. Current decreased with time, but the results demonstrated

clearly that the most severe galvanic couple is steel to steel. The 90-10 copper nickel to steel couple generated even less current than that for alloy 400 and the 70-30 copper-nickel. The International Copper Research Association (now the International Copper Association) further conducted several research programs clarifying and elaborating on these earlier findings [7, 8].

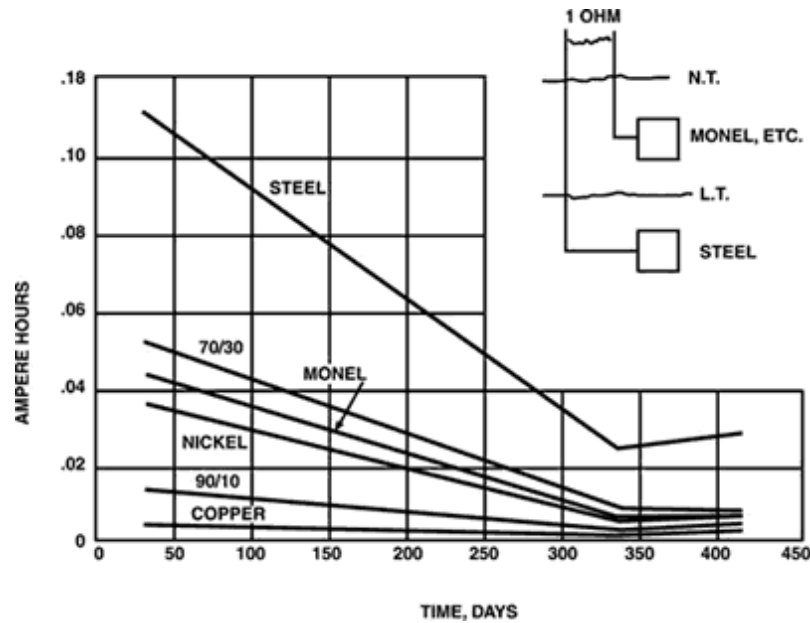


Figure 2. Total Current per Tide vs. Time between Alloy Plates connected to Steel in a Simulated Piling Test. [3]

In service it has been found that the galvanic interface between alloy 400 and the steelwork above the sheathing in the atmosphere is potentially the more severe site for galvanic corrosion as a result of the sea spray [4]. However, this area is more easily observable and a sound paint coating over the steelwork and interface can be maintained relatively easily.

Assessment of the corrosion rate of welded alloy 400 sheathing measured after 15 years showed evenly distributed shallow pitting of 0.025mm deep[4].

Alloy 400 Splash Zone Sheathing for Riser Pipes.

Riser pipes convey oil or gas to or from the sea bed and are particularly critical items. The conveyed fluid is usually at elevated temperature and under pressure so that excessive thinning by corrosion can culminate in a pressure burst leading to fire. Aramco first used 65% nickel-copper (Alloy 400) in the Arabian Gulf for legs and risers in the late 1950s, as reported by Hopkins [4]. An explosion on a platform occurred in the Middle Eastern Gulf in 1967 and a few years later in 1975 in the Ekofisk field in the North Sea. Both were caused by fracture of steel riser pipes initiated from cracking of their concrete cladding. The decision was made to sheath the replacement Gulf and other risers in 3mm thick alloy 400 and in a survey 10 years later was reported as giving excellent service [4]. In 1974, the Middle East experience led BP to specify 3mm for the risers in their North Sea forties platforms and the Ekofisk explosion led to Philips using 5mm sheathing.

The temperature of oil in the riser pipes can be higher than 90°C. On the other hand, the sea water in the North Sea is relatively cold with high oxygen content and heavy wave action.

This combination of factors can lead to very high steel splash zone corrosion rates; 7.5mm in 400 days was experienced by the fractured Ekofisk riser pipe [4].

The early experience has generally led to metal sheathing thicknesses of 3-5mm since with the sheathing welded into position. A common method is for half cylinders to be formed and welded to the riser pipe in the horizontal direction usually with a 3 bead technique to minimise dilution. Longitudinal seams are overlapped and welded so that there is no longitudinal weld directly on to the riser.

The sheathing is normally attached to extend to at least just below the mid tide level as this is the highest point at which cathodic protection is effective. Extension of the sheathing to a greater depth is required if there is no cathodic protection present in which case the sheathing should extend at least to just below the low-tide level. The upper level is a matter of economics but should preferably be taken to above the normal influence of wave action.

The feedback about the performance of 65% nickel-copper (Alloy 400) in splash zone applications over the last 50 years has been excellent [5]. Corrosion rates are minimal, the alloy is found to withstand sizeable impacts and tearing and the initially anticipated galvanic problems have not been realized in practice.

The authors are only aware of one type of problem area occurring in the North Sea since the 1970s. From 1987 to 1990, four riser failures occurred in 20 inch diameter risers on Forties field. Failure had occurred at the over-stressed fillet weld at the longitudinal seam due to the pressure build-up of hydrogen between the riser and the sheathing. Hydrogen had diffused through the steel riser causing a high pressure build up to such a high level that it caused mechanical damage of the sheathing. Wave action also introduced a fatigue element. The hydrogen was produced by internal corrosion of the riser due to poor inhibition of the wet oil and was later rectified [5]. Destructive testing failed to find any evidence of hydrogen embrittlement in the alloy 400.

Although alloy 400 has been found to resist corrosion extremely well in comparison with other splash zone protection at ambient temperature, no specific corrosion rates have been identified in the literature. At higher temperatures, it can be surmised that corrosion rates are higher than those experienced on legs. The alloy is a standard alloy for the construction of salt evaporators but these operate under essentially non-aerated conditions which are not strictly relevant. However, even in fully aerated 3% sodium chloride brine at 105°C, the corrosion rate of alloy 400 was 0.06mm/yr. Hopkins [4] surmised that the corrosion rate of the alloy on hot risers was likely to be between 0.01-0.03mm/yr under the most severe conditions.

90-10 Copper-nickel Splash Zone Sheathing

In the early 1980s, it was recognised that 90-10 copper-nickel could offer a valid alternative to alloy 400 in terms of corrosion resistance. This had an added potential advantage in that it could also provide resistance to macrofouling. Copper-nickel alloys have an inherent high resistance to macrofouling as long as they are insulated from less noble alloys or cathodic protection.

If the emphasis for copper-nickel sheathing is corrosion resistance, the alloy can be welded to the steel legs or risers in a similar manner to alloy 400 and should at least span from below mean tide level to well into the atmospheric zone. Potential galvanic corrosion on the adjacent steel is addressed by coating the more accessible top section with paint. Although the early trials in ambient sea water, already described, indicated that accelerated corrosion at the submerged junction is not enhanced by the presence of the sheathing, the area will normally be protected by the cathodic protection system routinely applied to the structure anyway.

Sheet thicknesses for legs of 3-5 mm would normally be recommended. The sheet is pre-formed to half cylinders and longitudinal joints are lapped so that the alloy is welded to itself. These require a 70-30 copper-nickel weld consumable. Horizontal butt welds between sections can be made direct to the steel and are often a 3-bead method such that the cap experiences minimum dilution from the steel. 65% nickel-copper or appropriate nickel consumables are required for the root runs on circumferential welds or fillet welds of copper-nickel to steel to withstand the high levels of iron dilution from the steel and avoid hot cracking. Where the steel has a rough surface or it is not considered appropriate to weld the alloy sheathing direct to the steel riser or structure, horizontal steel bands can initially be welded to the steel and the sheathing welded to the band. An outline of a typical cladding assembly recommendation is shown in Figure 3 with an indication of the types of joint involved and the weld procedure.

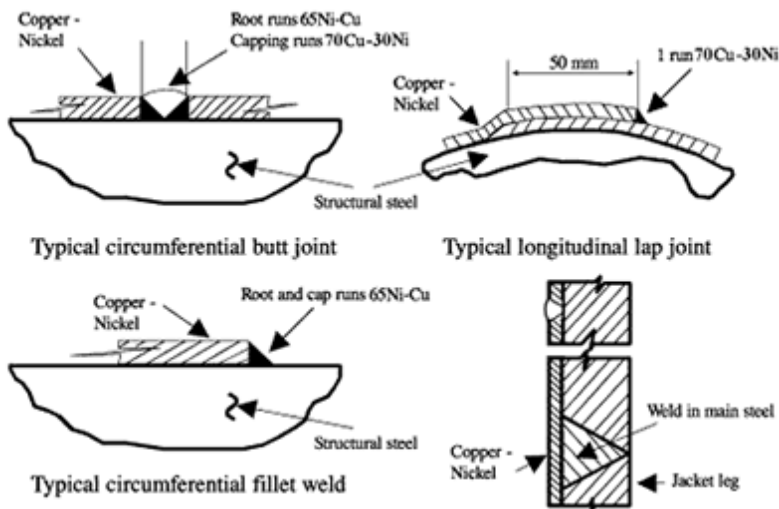


Figure 3. Typical joints for splash zone sheathing [9, 10]

Stage 1 of the Morecambe Field in the Irish Sea was the first major project to make use of the copper-nickel sheathing concept, the prime reason being to make use of its corrosion resistance. Copper-nickel was used to cover legs on production and accommodation platforms, three drill platforms and a flare stack.

For the Morecambe Field, the sheathing was 4mm thick annealed sheet, welded directly to the steel, and spanned +13m to -2m Lowest Astronomical Tide. Longitudinal overlap seams were specified using a MONEL 67 (70-30 Cu-Ni) consumable. Circumferential seams were welded direct to the steel using in this case the high nickel, Nickel 61, consumable with capping runs in MONEL 67. The legs were cathodically protected.

The Morecambe Field jackets have been inspected at intervals since they went into service and the performance of the copper-nickel has been excellent. Underwater video records of the condition of the steel and sheathed splash zone regions have been taken and show good performance of the copper-nickel sheathing. There is no significant corrosion of the copper-nickel sheath or adjacent steel. With the cathodic protection, marine fouling has occurred on the copper-nickel since it is welded directly to the steel, but comments after 12 years service indicated that this was light compared to the steel below the sheath where heavy mussel

fouling and soft hydroid growth ranging from 40 to 90 mm thick is seen. Divers at that time also commented that the fouling is more loosely attached to the copper-nickel and easy to remove with a hand scraper [11].

LaQue Copper-Nickel Trials

Findings from the Morecambe Field correspond well to the expectations given by more recent LaQue Center trials. The copper industry wished to examine the performance of copper-nickel sheathing more closely and initiated long term exposure trials at two sites, co-ordinated by the LaQue Center for Corrosion Technology examining various types of attachments to steel pilings which would evaluate both corrosion and biofouling behaviour. Despite the ravages of extreme weather including hurricanes to which the exposure sites in North Carolina are prone, the pilings survived and when the test sites were finally abandoned after 16 and 20 years, final long-term investigations were carried out and have been reported[1].

Forty ASTM Type A-36 steel pilings 17 cm in diameter were sheathed with 4.6 mm thick x 3 m long 90-10 copper-nickel. Some copper-nickel sheaths were directly welded to the steel; others were insulated from the steel with concrete or with 6 mm of a butyl rubber compound. Some pilings were cathodically protected with Galvalum III anodes while others remained unprotected. Pilings were removed after two years, five and ten years of exposure in a natural flowing seawater channel for evaluation. A final evaluation was made when the site was abandoned after 20 years.

The test programme compared levels of fouling on electrically insulated vs. non insulated Cu-Ni sheathing, anode consumptions with and without sheathing, corrosion rates of steel behind the sheathing and the sheathing itself, galvanic attack at the top and bottom steel/sheathing junctions when welded in position. Alloy 400 sheathing was also included for comparison.

There was no measurable loss of thickness of the copper-nickel sheathing itself in the case of the directly welded and insulated pilings. Measurements for steel were taken on the submerged areas of the cathodically protected sheathed piles after exposure. These showed that corrosion losses were comparable to those at the corresponding areas on the cathodically protected bare steel controls. The mass of biofouling accumulation on the sheathing that was electrically insulated from the steel was 1-4% of that present on the bare steel after 10 years exposure and low levels of fouling continued through 20 years. Pilings with the directly welded sheathing accumulated less than 40% of the biofouling mass compared to the bare steel controls.

The sheathing also reduced the anode consumption rates particularly for 5 and 10 year removals. The most significant reduction was for the insulated sheathing, presumably because the concrete reduced the area of metal requiring cathodic protection. The anode consumption associated with the directly welded sheathing was lower than for the bare steel and the corresponding anode output was lower. This is considered to be due to the favourable polarisation behaviour of the 90-10 copper-nickel alloy and is in accordance with the early trials described. The potentials indicated satisfactory levels of cathodic protection throughout the test.

Corrosion at the sheathing/steel atmospheric junction eventually (15 years) perforated the steel pipe in both the alloy 400 sheathed and direct welded 90-10 copper-nickel sheathed pilings re-emphasising it is important to maintain coatings at the steel/sheathing interface at the top of the sheathing.

Existing Data for 90-10 Copper-Nickel in Hot Seawater.

A review of the effect of temperature and heat transfer for 90-10 copper-nickel was made in reference [12] and looked at ambient to 150°C. In general, temperature had only a moderate effect on the corrosion rate in sea water but the relationship was irregular, assumed to be due to variable factors including pre-existing surface films, flow velocity and pollutants. Much data has been obtained with MSF desalination practices in mind. The corrosion rates are low but the data is of limited value for the splash zone application as the hotter processes in MSF desalination involve de-aerated brines. However, some data [13] looked at the effect of oxygen pick up to 200ppb at 104°C, Figure 4. The corrosion rate of aluminium brass (C68700) was found to be more sensitive to changes in low concentrations of oxygen than 90-10 and 70-30 copper-nickels.

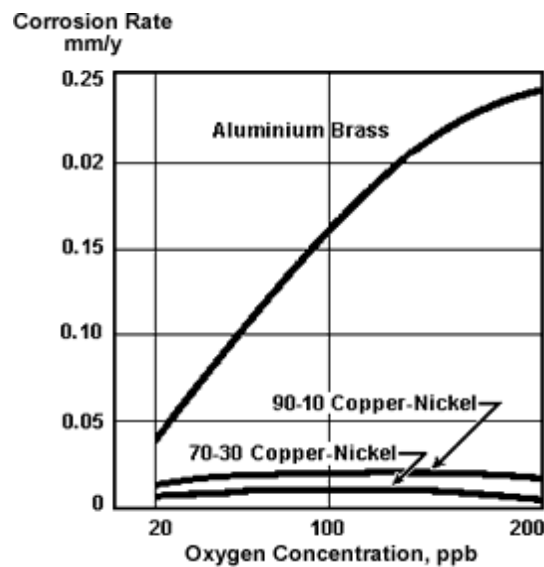


Figure 4. Effects of oxygen concentration on the corrosion of three copper alloys in deaerated seawater (90 days at 104°C T.D.S. = 35,000 ppm)[13]

Smith and Compton [14] looked at the galvanic potentials of several alloys including alloy K 500(an age hardenable version of alloy 400 with similar corrosion resistance), 90-10 and 70-30 copper-nickels and 1016 steel at temperatures up to 200C in both aerated and de-aerated sea water. Galvanic series were produced at 30°C, 100°C, and 160°C in aerated sea water using an autoclave. The median potentials measured for the alloys of interest in aerated sea water are shown in Table 1. The general effect of increased temperature was to increase the electro-negativity of alloy K500 and both the copper-nickels. The steel, however, had shown a small decrease in potential at 100°C before increasing again at 160°C.

Table 1 Median potential values in millivolts vs SCE taken from [14]

| Temperature | Alloy K500 | 90-10 Cu-Ni | 70-30 Cu-Ni | Steel 1016 |
|-------------|------------|-------------|-------------|------------|
| 30 °C | -160 | -230 | -220 | -675 |
| 100 °C | -230 | -340 | -300 | -700 |
| 160 °C | -260 | -420 | -395 | -640 |

This indicates that higher temperature will decrease the relative differences in galvanic potential between the alloys and steel.

Experimental Setup

From the Morecambe field experience, it is clear that copper-nickel sheathing can provide effective splash zone sheathing for legs. More confidence was required however to justify its use for risers given hot metal temperatures are in contact with relatively cold, aerated sea water.

Assessment work was carried out by Materials Engineering Research Laboratory Ltd, UK [15], and involved primarily 90-10 copper-nickel although limited testing of 70-30 copper-nickel and alloy 400 were included for comparison. The samples were nominally 5mm thick and cut into five samples 76mm x 76mm. Appropriate numbers of 8mm diameter holes were drilled for hanging on a polymeric rack. The samples were exposed in substitute ocean water to ASTM D1141 at 100C with oxygen bubbled through the solution. The tests were performed in three reflux condensers, using one alloy per condenser, which cooled the water vapour generated and returned it to a tank. The five samples of each alloy were held in a vertical position with 3 of the samples completely immersed and 2 samples half immersed and half above the water line for each set of alloys. A simple polymeric rack was made to hold the test samples. The oxygen bubble stream was not directed towards the surface of the samples.

Figure 5 shows the apparatus and arrangement of samples. The exposures were run for a total of 1000 hours per set of samples, changing the salt solution weekly.

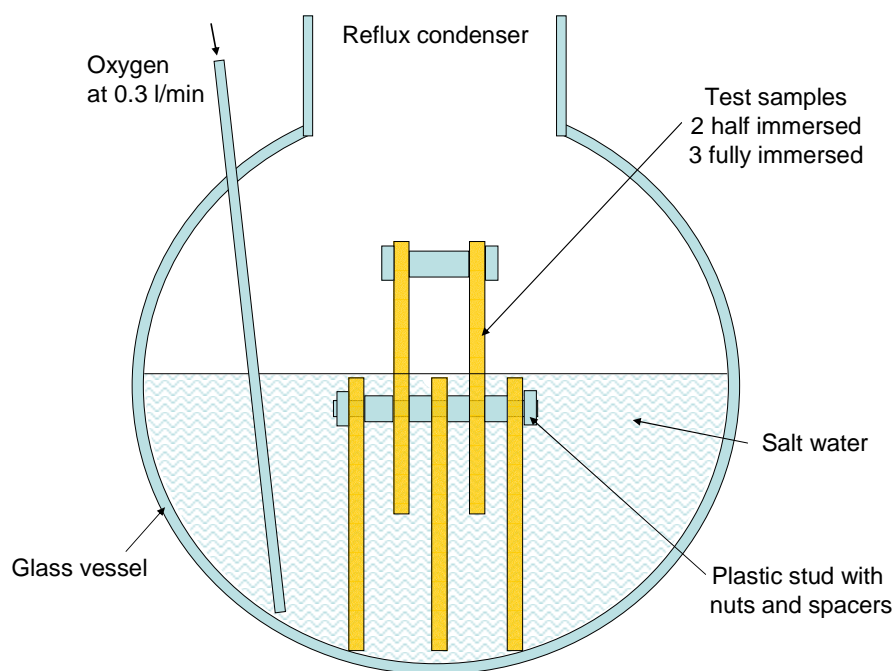


Figure 5. Schematic of Apparatus and Specimen Arrangement

The tests were performed to ASTM G31, Standard Practice for Preparing, Cleaning and Evaluating Corrosion Test Specimens Mass loss and Pitting, and were monitored after one, two and six weeks. The two other materials were weighed as a set and the mass change taken over the set of 5 samples

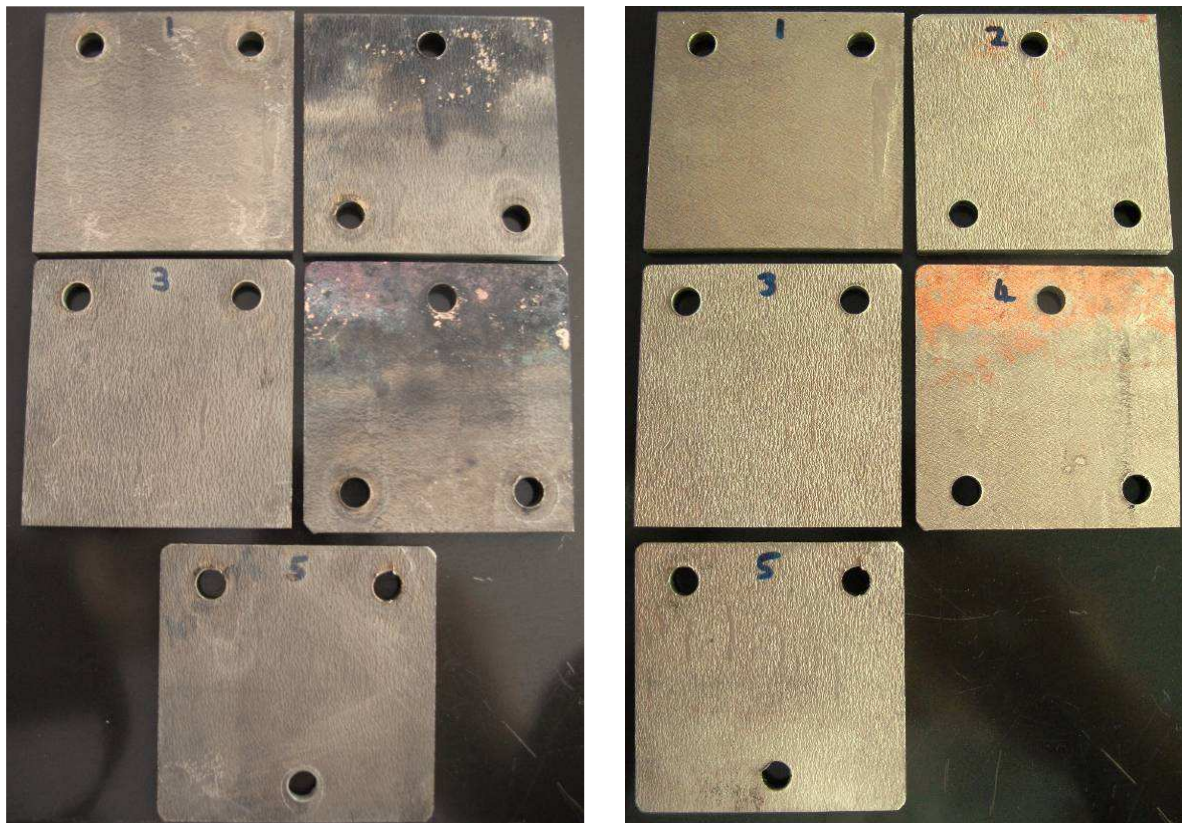
After the 1000 hours exposure, the samples were inspected and then cleaned in an ultrasonic bath using a 10% citric acid solution at ambient temperature. The samples were left in the ultrasonic bath for 30 minutes and then removed and reweighed.

For each material, three more samples which had not been exposed were also weighed, cleaned in the ultrasonic bath and reweighed to act as control samples for the cleaning process. Weighing was performed by a calibrated mg electronic balance. Pitting was assessed by visual and microscopic inspection. Follow up metallography and EDX analysis were carried out at the laboratories of KME in Osnabruck, Germany.

Results

Optical and Metallography

Figures 6 and 7, 8, 9 and 10 and 11 show the condition of 90-10 copper-nickel, 70-30 copper-nickel and 65% nickel-copper alloy 400 respectively after 6 weeks exposure, before and after ultrasonic cleaning. Samples 1, 3 and 5 show the immersed samples and 2 and 4 show the half submerged samples for each alloy.



Figures 6 and 7. 90-10 copper-nickel samples after 6 weeks exposure; before and after cleaning

The exposed samples of 90-10 copper-nickel showed a uniform colour when fully submerged but had a darker grey surface film in areas above the water for the partially submerged samples. After ultrasonic cleaning in citric acid, the darker grey surfaces had partially turned a coppery colour. No pitting on the bulk surfaces or crevice corrosion under the washers could be identified.

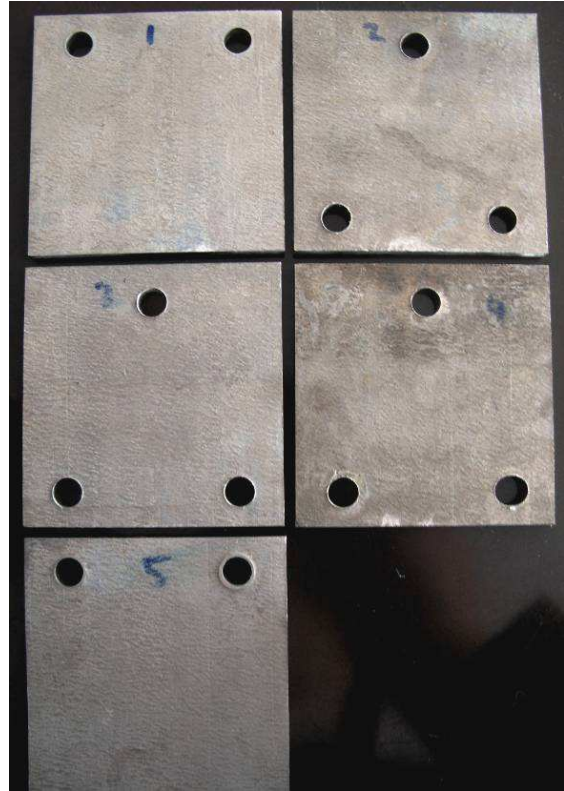


Figure 8 and 9. 70-30 copper-nickel samples after 6 weeks exposure; before and after ultrasonic cleaning.



Figure 10 and 11. Nickel-copper alloy 400 samples after 6 weeks exposure; before and after cleaning

The 70-30 copper-nickel had a grey appearance after exposure on both submerged and partially submerged specimens. There was a tinge of a brown colouration on the upper sections of the partially submerged samples which were removed by cleaning. No coppery deposits were visible after cleaning. Again, on close inspection no pitting or crevice corrosion could be found.

The as-exposed, submerged samples in alloy 400 were fairly uniform in surface appearance after the 6 weeks exposure but the partially submerged samples showed a green surface film in the areas above the submerged zones. After cleaning the green film disappeared. Some areas when examined in close up appeared pitted especially on the splash zone surfaces of metals which were partially submerged, see figure 12, and there were signs of crevice corrosion on the submerged samples under the fastener washers, Figures 10,11,13.

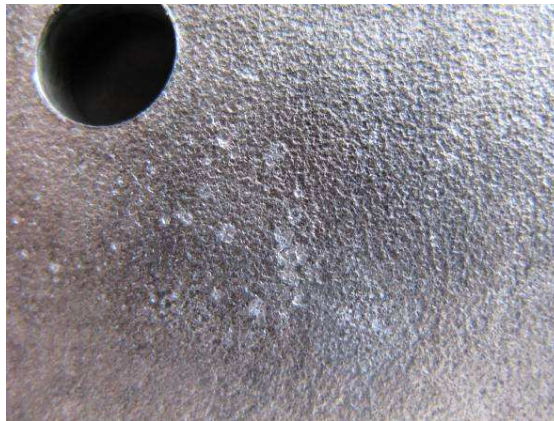


Figure 12. Close-up images of surfaces of typical nickel-copper alloy 400 samples after 6 weeks exposure and ultrasonic cleaning showing evidence of pitting.

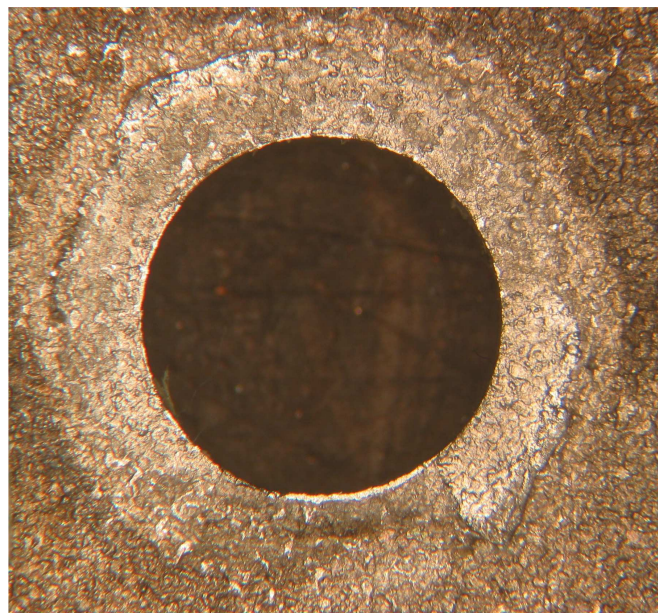


Figure 13. Close up of crevice corrosion in alloy 400

Metallography of sections through the coppery coloured areas of the 90-10 alloy showed a smooth surface not representative of denickelification although EDX analysis of the deposit confirmed copper. Evaluation of an off cut of the original unused material did not show copper on the surface but had the same microstructure. It appeared therefore that the citric acid had reacted with the surface film formed in the upper areas of the exposed partially submerged samples to form copper. Subsequent cleaning trials in sulphuric rather than citric acid totally removed the copper.

Metallographic sections through the exposed alloy 400 samples showed a shallow layer of cold work at the surface suggesting a light rolling pass as the final production process. It was not possible to definitely confirm pitting corrosion from the microstructures. EDX analyses of the 70-30 and alloy 400 surfaces revealed high silicon and oxygen peaks. These had not been apparent on the 90-10 alloy and are not easily explained as the analysis of the substitute sea water does not contain silicon.

Weight Measurements

The weight measurements and percentage gain and losses for the 90-10 alloy specimens are given in Table 2. The corrosion rates calculated from these figures are given in the final row.

The weights of the specimens relative to the initial weight increased with the time of exposure as the oxide films formed and developed. When cleaned, the weight dropped compared to the initial weight as the films were removed. The corrosion rate was calculated from the original weights and the final cleaned specimens. The corrosion rates of the partially submerged samples would be expected to be higher if the coppery deposits had been fully removed by the cleaning process.

Table 2. Weight loss, g, for 90-10 samples over 6 week exposure

| | Sample No. | | | | |
|------------------------------------|----------------------|----------------------|-----------------------|-----------------------|----------------------|
| | 1 | 2 | 3 | 4 | 5 |
| Submerged | Full | Partial | Full | Partial | Full |
| Initial | 267.317 | 262.154 | 265.343 | 264.658 | 262.073 |
| 170hrs | 267.341 (+0.009%) | 262.164 (+0.004%) | 265.354 (+0.004%) | 264.664 (0.002%) | 262.086 (+0.005%) |
| 500hrs | 267.367 (+0.019%) | 262.216 (+0.024%) | 265.361 (+0.007%) | 264.701g (+0.016%) | 262.091 (+0.007%) |
| 1000hrs | 267.395 (+0.029%) | 262.211 (+0.022%) | 265.374g (+0.012%) | 264.692g (+0.013%) | 262.114 (+0.016%) |
| 1000hrs After u/s clean | 267.220 (-0.036%) | 262.007 (-0.056%) | 265.218 (-0.047%) | 264.411 (-0.093%) | 261.950 (-0.047%) |
| Corrosion rate mm/a | 0.007 | 0.011 | 0.009 | 0.018 | 0.009 |

The 70-30 copper-nickel and alloy 400 samples 1-5 were not weighed individually prior to testing and so could not be used as an accurate weight loss comparison.

Discussion

In general terms, copper-nickels would normally be expected to have a better resistance to localised corrosion in terms of pitting and crevice corrosion than alloy 400 in sea water environments [16]. All alloys would be expected to be immune to chloride stress corrosion cracking. The results obtained from this test programme are consistent with this.

For copper-nickel alloys, the surface films formed in sea water are complex and protective, and are known to mature with time such that the corrosion rate decreases [17]. Good film formation is a pre-requisite of good corrosion resistance. More salts from the sea water would be expected to concentrate on the upper areas of the partially submerged samples as they would not be so effectively washed and different film formation would be expected in the two areas. This appears to have occurred in these trials.

The cleaning procedure only succeeded in partially removing the surface films and deposits on the samples; particularly the 90-10 alloy. The combination of this and the limiting measurements possible from the assemblies of the 70-30 and alloy 400 samples do not allow an accurate indication of the relative weight loss of the alloys to each other. For a fuller understanding, this preliminary work requires further, more detailed, comparison work on the 70-30 and alloy 400 specimens. Nevertheless 90-10 copper-nickel proved to have good resilience to high temperatures in aerated sea water and excellent resistance to pitting and crevice corrosion. There is every indication that it can be expected to perform at least as well as alloy 400.

Conclusion

90-10 copper-nickel has enjoyed over 20 years excellent service as splash zone sheathing welded onto the legs of Stage 1 platforms in the Morecambe Field. Substantial economies could be made if the alloy could be used instead of the established alloy Nickel-Copper alloy 400 for sheathing hot risers in future offshore projects. There is no indication in the literature to suggest that copper-nickel is not capable of performing well for this application but more data was required to provide a higher degree of confidence.

Preliminary testing has been carried out in aerated synthetic ocean water at 100°C using a reflux condenser test assembly for 1000hours. 90-10 and 70-30 copper-nickel samples were evaluated, with particular emphasis on the 90-10 alloy, and compared to alloy 400. Both copper-nickel alloys performed well and showed no pitting or crevice corrosion. Crevice corrosion and some indication of pitting was found on the alloy 400. Further evaluation of weight loss will be required to provide a comparison between general corrosion rates of alloy 400 and copper-nickel. The work to date however gave every indication that the 90-10 or 70-30 alloy would give at least equivalent service to alloy 400 in hot riser applications.

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References

1. C. Powell and H. Michels, Review of Splash Zone Corrosion and Biofouling of C70600 Sheathed Steel During 20 Years Exposure. Eurocorr **2006**.
2. Engineering Equipment and Materials User Association, 90/10 Copper Nickel Alloy Piping for Offshore Applications, Specification: Tubes Seamless and Welded, Publication No. 144, **1987**.
3. R.W. Ross, Jr and D.B. Anderson, Proceedings of the 4th International Congress on Marine Corrosion and Fouling, **1976**, pp461-473

4. D.J. Hopkins, MONEL Alloy 400 Sheathing for Complete Splash Zone Protection. Offshore Europe 77, Aberdeen, 1977.
5. D.T Peters, H.T Michels, C.A.Powell. Metallic Coatings for Corrosion Control of Marine Structures. Internal Workshop on Control for Marine Structures and Pipelines, Galveston, Texas. **1999**.
6. W. Kirk, Materials Performance, **1987**, Vol. 26, 9, pp23-28.
7. H. Arup. Cathodic Current Demand of Copper-nickel Sheathed Piling. Danish Corrosion Centre. INCRA project 371.
8. J.A. Ellor and G.A. Gehring Jr. Galvanic Corrosion of Copper-nickel Sheathed Steel Piling. Ocean City Research Corp. INCRA project 368. March **1987**
9. D.E. Jordan and C.A. Powell, Proc. International Conference on Welding in Maritime Engineering, Croatian Welding Society and SLV Munchen GmbH, **1998**, pp171-181.
10. Copper Development Association, Publication 139. **1999**
11. Personal communication, British Gas.1993
12. M.S. Parvizi et al. International Materials Review, **1988**, Vol 33, 4. pp169-200
13. A. Tuthill, B. Todd, J. Oldfield, IDA World Congress on Desalination and Water Reuse, Paper No 73. Vol. III. **1997**, p251
14. C.A. Smith and K.G. Compton, Corrosion Vol. 31 No. 9 Sep. **1975**. pp.320-326
15. P. Hansen and M. Lewan. Corrosion Testing of Cu/Ni alloys. MERL Report C2076-1 **2007**
16. A. Tuthill and C. Schillmoller, INCO Publication, Guidelines for Selection of Marine Materials. **1971**
17. C. Powell and H. Michels, Copper-Nickel Alloys for seawater corrosion resistance and antifouling-A State of the Art review. Corrosion 2000, NACE. Paper 627