Technical Report

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Metallic Coatings for Corrosion Control of Marine Structures

A1213-XX/99

Copper Development Association Inc.

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Carol A. Powell

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Abstract

The use of metallic coatings including copper-nickel alloys, nickel-copper and stainless steel, particularly in the spray/splash zone, is a proven and valuable engineering method for corrosion protection of marine structures. The excellent performance of the copper-nickel alloys in terms of both corrosion and biofouling resistance in marine environments suggests these alloys for the protection of offshore structures and ship hulls. Sheathing techniques have been developed for both applications and some service experience has been gained on 90-10 copper-nickel (C70600), 70-30 copper-nickel (C71500) and 70-30 nickel-copper (Alloy 400). Furthermore, 70-30 nickel-copper (Alloy 400) sheathing has been utilized on legs and risers of oil and gas platforms in several parts of the world. This paper reviews the properties of the copper-nickel alloys including the corrosion behavior and biofouling resistance as affected by composition, water velocity, exposure conditions and methods of attachment to steel. The mechanisms of offshore structure corrosion are reviewed, leading to discussion of the most effective use of a copper-nickel protective sheath. Results of a number of long term trials of copper-nickel alloys applied to pilings as well as ship hulls are described. Cost benefits due to reduced maintenance and to reduced structure size and weight through elimination of splash zone corrosion allowance and to lower wave forces on the structure have been analyzed. Methods of application of copper-nickel alloy sheet to platform structural members, and alternative resin-particulate containing copper-nickel sheet formulations are discussed.

Key terms: seawater corrosion, copper-nickel alloys, nickel-copper alloys, stainless steels, metallic coatings, offshore structures, biofouling

Introduction

Marine engineers have long sought effective and economical means to protect structures from the ravages of seawater corrosion and marine biofouling. A broad range of coating systems, some with antifouling properties, have been developed and are the most commonly used approach to protecting steel structures, ship hulls in steel, wood, glass fiber reinforced plastics (GRP) and aluminum, as well as concrete, wood pilings, etc. Coatings will of course continue to be used including the cupric oxide and organotin antifouling paint systems although the latter has been banned in many countries because of their high toxicity to marine life. Where extremely long life with freedom from maintenance is required, use of metallic sheathing has proved to be a sound engineering approach. A variety of alloys including stainless steels, 70-30 nickel-copper (Alloy 400) and the copper-nickel alloys have been applied. The copper-nickel alloys are particularly attractive for marine structure sheathing because they provide corrosion protection and at the same time resist the build up of the thick biofouling mass that degrades the performance, structural integrity, and even the safety of the structure. In addition, copper-nickel alloys reduce maintenance costs by minimizing the need to remove biofouling on a regular basis as well as eliminating the need for periodic reapplication of biofouling-resistant paints and coatings.

This paper first briefly reviews the properties of the copper-nickels and nickel-copper (Alloy 400) that recommend them for use as sheathing materials. It then discusses galvanic effect issues arising due to the relatively noble sheathing alloys in contact with the steel structures and finally describes a number of successful installations and sheathing systems applicable to offshore structures or to ship hulls.

The Copper-Nickel Alloys

Alloy Compositions

Of the several copper-nickel alloys, two alloys are extensively used in marine applications including piping, condensers and desalination plants; the 90% copper-10% nickel (90-10) alloy and the 70% copper-30% nickel (70-30) alloy. These are denoted C70600 and C71500 respectively in the Unified Numbering System used in the United States and Canada. Both alloys contain iron and manganese additions to improve impingement and localized corrosion resistance. Manganese additionally functions as a deoxidizer and is intentionally added for that purpose when the alloy is being melted. When comparing the various specifications used worldwide, the compositional ranges of the two alloys vary slightly from one specification to the next, as shown in Table I.

TABLE I
COMPARISON BETWEEN VARIOUS SPECIFICATIONS FOR 90-10 AND 70-30 COPPER NICKEL ALLOYS

(Maxima except where range given)

		90-10			
		ISO	BS	ASTM	DIN
		CuNi10FelMn	CN 102	C70600	CuNi10Fe 2.0872
Copper					
	min	Rem	Rem	Rem	Rem
	max				
Nickel					
	min	9.0	10.0	9.0	9.0
	max	11.0	11.0	11.0	11.0
Iron					
	min	1.2	1.0	1.0	1.0
	max	2.0	2.0	1.8	1.8
Manganese					
	min	0.5	0.5	-	0.5
	max	1.0	1.0	1.0	1.0
Tin					
	min	-	-	-	-
	max	0.02	-	-	-
Carbon		0.05	0.05	0.05*	0.05
Lead		0.03	0.01	0.02*	0.03
Phosphorus		-	-	0.02*	-
Sulphur		0.05	0.05	0.02*	0.05
Zinc		0.5	0.5	0.5*	0.5
Total Other Impurities		0.1			0.1
Total Impurities		-	0.3	-	-

		70-30			
		ISO	BS	ASTM	DIN
		CuNi30MnlFe	CN 107	C71500	CuNi30Fe 2.0882
Copper					
	min	Rem	Rem	Rem	Rem
	max				
Nickel					
	min	29.0	30.0	29.0	30.0
	max	32.0	32.0	33.0	32.0
Iron					
	min	0.4	0.4	0.4	0.4
	max	1.0	1.0	1.0	1.0
Manganese					
	min	0.5	0.5	-	0.5
	max	1.5	1.5	1.0	1.5
Tin					
	min	-	-	-	-
	max	0.02	-	-	-
Carbon		0.06	0.06	0.05*	0.06
Lead		0.03	0.01	0.02*	0.03
Phosphorus		-	-	0.02*	-
Sulphur		0.06	0.08	0.02*	0.05
Zinc		0.5	0.5*	0.5	
Total other Impurities		0.1			0.1
Total Impurities		-	0.3	-	-

*When required for welding

These variations have little influence on the service performance of the alloys. Iron is essential for both 90-10 and 70-30 copper nickel because it provides added resistance to erosion-corrosion caused by moving seawater, which is especially important to pipe systems. These two elements, iron and to a lesser extent, manganese, increase the shear force (from the flowing seawater) required to remove the protective oxide. The beneficial effect of iron content on the impingement attack on 90-10 copper-nickel from 30-day tests at 3 m/s water velocity has been verified.[1] A distinct minimum is apparent between 1.5 and 2.5% iron. It is generally believed that iron should be in solid solution to be effective and provide maximum impingement corrosion resistance; i.e., the material must be cooled relatively rapidly after hot rolling or annealing. However, impingement corrosion is not a large issue in sheathing applications and therefore whether or not the iron is in solution is not a concern. The composition of 70-30 nickel-copper (Alloy 400) is given in Table II.

TABLE II

COMPOSITION OF 70-30 NICKEL-COPPER (ALLOY 400) - IN WEIGHT %*
(Maxima except where range given)

Nickel	
min	63.0
Copper	
min	28.0
max	34.0
Iron	2.
Manganese	2.0
Carbon	0.3
Sulfur	0.024
Silicon	0.5

*Specifications Include UNS N04400; ASTM B127, B 163-B165, B 564; DIN 17743, 17750-17754, BS 3072-3076 (NA 13)

Mechanical Properties

Typical annealed mechanical properties of the two copper-nickel alloys and the one nickel-copper alloy are shown in Table III.

TABLE III

TYPICAL MECHANICAL PROPERTIES OF COPPER-NICKEL AND NICKEL-COPPER ALLOY 400
(As Hot Rolled)

Property	90-10	70-30	Alloy 400
Yield Strength, MPa (0.5% ext.)	110	138	240*
Tensile Strength, MPa	303	379	550
Elongation, %	42	45	40

* 0.2% offset

Strength increases with nickel content. These three alloys are single phase, solid solution strengthened and are not hardenable by heat treatment. Strength can be increased by work hardening and is an effective means of strengthening drawn products such as tube, rod or wire. A smaller amount of strengthening by cold work is possible for the wide plate required for ship hull or offshore structure sheathing and can be helpful in regard to durability.

The high strength and ductility of the copper-nickel alloys give assurance that a sheathed steel jacket member will withstand normal impact, erosion and abrasion that might be experienced in service operations on a platform.

Corrosion Resistance

Metals and alloys are subject to several forms of corrosion in seawater including general wastage, impingement attack and localized corrosion, such as pitting, crevice corrosion, stress corrosion cracking and intergranular attack. The continued use of copper-nickel in alloys over many years in seawater has confirmed their good resistance to the wide variety of these forms of corrosive attacks.

General Corrosion. General corrosion rates for 90-10 and 70-30 copper-nickel alloys in seawater are low, ranging between 0.025 and 0.0025 mm/yr[2]. For the majority of applications, these rates would allow the alloys to last the required lifetime, and there would be little probability of their premature failure in service due to such a corrosion mechanism.

Fourteen years of data collected at the LaQue Center for Corrosion Technology at Wrightsville Beach, North Carolina USA, for 90-10 and 70-30 alloys[3] in quiet seawater, flowing seawater (0.6 m/s), and tidal conditions are shown in Figure 1.

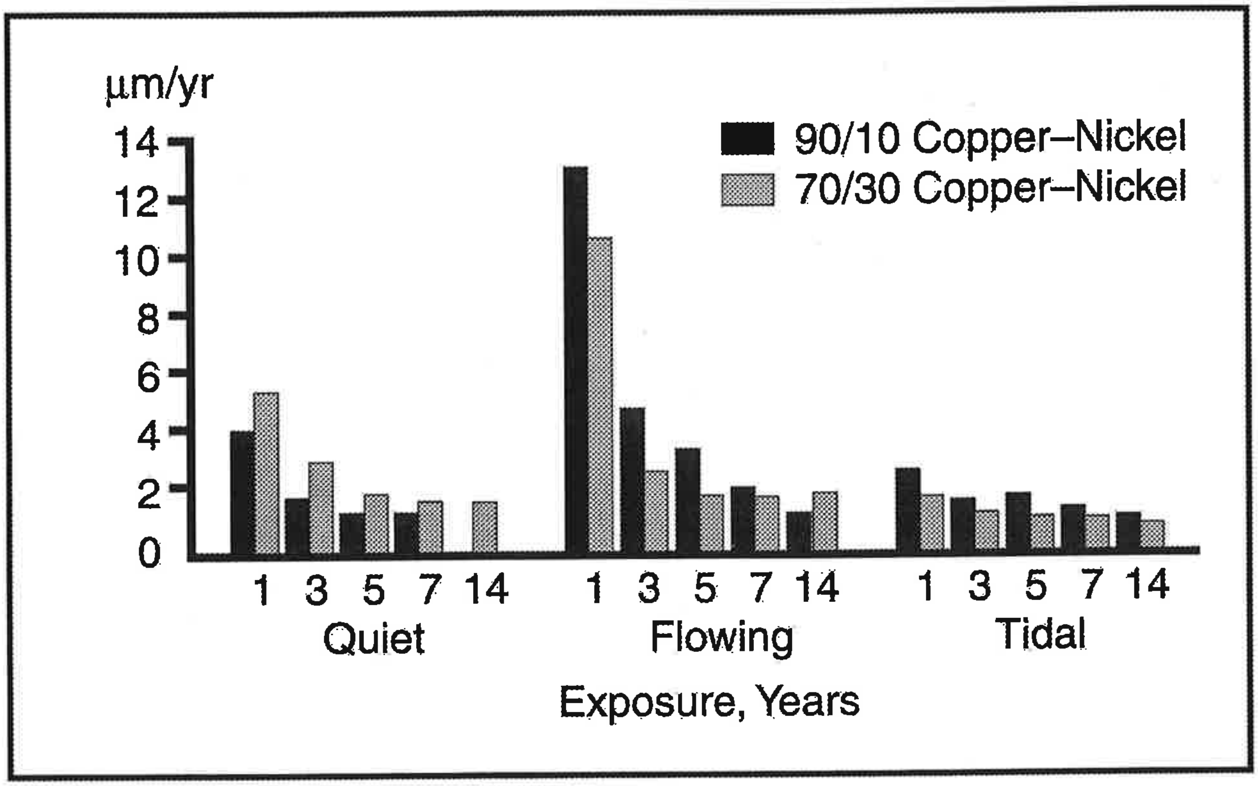

Figure 1 The change in corrosion rate with time for 90-10 and 70-30 Copper-nickel in quiet, flowing and tidal zone seawater.

It was found that, in all instances, corrosion rates were higher during early stages of testing, before stabilizing of their protective corrosion films and then decreases as these films mature. The highest initial corrosion rates were found in flowing seawater; although in the latter years of testing, the corrosion rates for 90-10 were similar in all the conditions. For 70-30 copper-nickel, this trend of decreasing corrosion rates with increasing time, was true for quiet as well as flowing conditions, but corrosion rates were consistently lower for tidal conditions throughout. In summary, both alloys exhibit parabolic film growth and low general corrosion rates.

<u>Localized Corrosion.</u> Alloys, such as stainless steels, are protected by a passive film and tend to have low general corrosion rates. However, they can suffer localized corrosion once their films are damaged. This occurs in susceptible alloys, particularly at velocities of less than 1 m/s when marine-fouling attachments can form additional crevice sites. At higher velocities, marine organisms have difficulty becoming attached.

Copper-nickels have advantages over some other alloy types by having a high resistance to biofouling, thereby decreasing the number of potential sites where localized corrosion could occur. The copper-nickels also have a high inherent resistance to pitting and crevice corrosion in quiet seawater. Sixteen-year tests[4] on 70-30 copper-nickel alloy reported the average depth of the twenty deepest pits to be less than 0.127 mm. When pits do occur, they tend to be shallow and broad in nature and not the undercutting type of pitting which can be expected in some other types of alloys.

Crevice corrosion seldom occurs in copper-nickel alloys and little data is published about the phenomenon.[1]

The copper-nickels are generally immune to chloride-and sulphide-stress corrosion cracking in seawater and have a high resistance to stress corrosion cracking due to ammonia in seawater service.

Galvanic Effects. Copper-nickel alloys are fairly central in the galvanic series. They are: less noble than titanium, nickel-copper alloys and stainless steels; compatible with other copper-based alloys; and more noble than steels. The 70-30 copper-nickel alloy is slightly more noble than the 90-10 alloy. Therefore the 70-30 copper-nickel alloy is frequently used as the weld filler metal in welding the 90-10 alloy.

Protective Film Formation. The good corrosion resistance in seawater offered by copper-nickel alloys is a direct consequence of the formation of protective oxide films on their metal surfaces. These films form naturally and quickly following the initial exposure of these alloys to seawater.

In clean seawater, the film is predominantly cuprous oxide, and its protective value is enhanced by the presence of nickel, iron and manganese. Cuprous hydroxy-chloride and cupric oxide are often also present.[4,5] The film can be brown, greenish-brown or brownish-black. In 90-10 copper-nickel, the film thickness can be on the order of 4400 A.[1,5]

The rate of film formation was characterized by Tuthill[5], from the measurements of the copper content of condenser seawater effluent, over a three-month period after start up. Copper content was found to decrease from 10 to 1 ppm in ten minutes and further to 0.1 ppm in an hour. After three months, the copper in the effluent was at virtually the same level as that in the intake water, which is below 0.01 ppm. This indicates that the growth or maturation of the protective film, over time results in a reduction in the corrosion rate of the 90-10 copper-nickel condenser alloy tube surfaces.

The film, however, continues to become even more protective with time, as indicated by corrosion rate measurements made over several years. Studies in quiet seawater show that the time span approaches four years before the decrease in corrosion rate becomes negligible. In flowing water, the corrosion rate, as shown in Figure 1, was found to decrease continually over at least a 14-year period, the effect being similar for both 90-10 and 70-30 copper-nickel alloys. The composition and properties of the film depend on the alloy composition and the condition of seawater at the time of initial exposure. In polluted seawater, any sulfides present can interfere with film formation, producing a black film containing cuprous oxide and sulphide[1]. This film is neither as protective nor as adherent as films formed in unpolluted water. However, if an established cuprous oxide film is present, periodic exposure to polluted water can be tolerated without damage to the protective film.

Effect of Velocity. The combination of low general corrosion rates and high resistance to pitting and crevice corrosion ensures that the copper-nickel alloys will perform well in quiet, clean seawater. As the flow rate of seawater increases, the corrosion rate remains low due to the adherent protective surface film on the alloys. However, once the velocity reaches a critical level, where the shear forces are sufficiently high to cause damage to the protective corrosion film, active underlying metal is exposed. This allows erosion-corrosion or impingement attack to occur. The seawater velocity at which this occurs is often called the "breakaway velocity" and different copper-based alloys show different breakaway velocities, as shown in Figure 2 prepared by Gilbert[6].

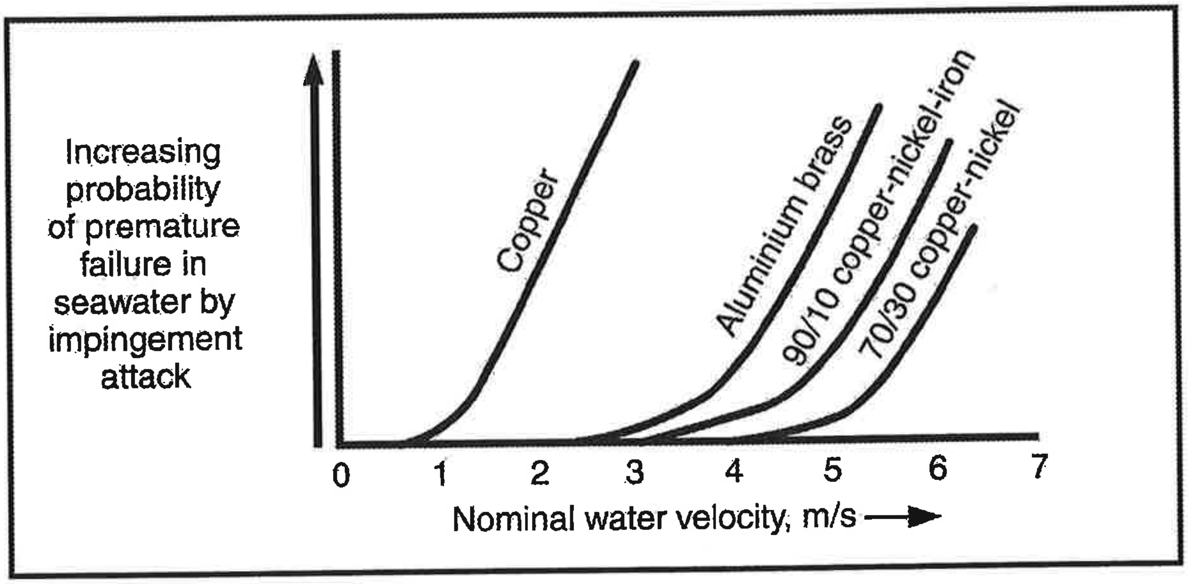

Figure 2 Velocity limitations for copper alloys in seawater.

Impingement corrosion is not a problem with copper-nickel alloys on fixed structures in seawater. Even with ship hulls protected with copper-nickel where the top speed significantly exceeds the nominal breakaway velocity of the 90-10 alloy, no erosion corrosion has been observed.[7,8,9] This is consistent with experiments done on larger diameter (102 mm) 90-10 copper-nickel pipe.[10] Resistance to seawater velocity of 7.3 m/s (the highest level obtainable in the experiment) was observed. This is consistent with the understanding of reduced shear stress at the pipe wall with increased pipe diameter at a given velocity. A planar ship hull can be viewed as a pipe of near infinite diameter.

Biofouling

Marine biofouling is commonplace in open waters, estuaries and rivers. It is commonly found on marine structures including pilings, offshore platforms, boat hulls, and even within piping systems and condensers. Fouling is usually heavier and more widespread in warm conditions and at low velocity (<1 m/s) seawater. At velocities above 1 m/s, most fouling organisms have difficulty attaching themselves to surfaces unless already secured. There are various types of fouling organisms including plants such as slime algae and sea mosses, sea anemones, as well as barnacles and mollusks such as oysters and mussels. On steel, polymers, and concrete marine construction, biofouling can be a very severe problem, resulting in unwanted excess drag on structures and marine craft in seawater, high wave loading on fixed structures such as pilings, or blockages in pipe systems. Expensive removal by mechanical means is often required. Alternatively, costly prevention methods are employed, which include chlorination of piping systems or antifouling coatings on structures.

Marine organisms attach themselves to some metals and alloys more readily than they do to others. Steels, titanium and aluminum will foul readily. Copper-base alloys, including copper-nickel, have very good resistance to biofouling, and this property is used to advantage. In the case of copper-nickel, it is used to minimize biofouling on intake screens, seawater piping systems, water boxes, cladding of pilings and mesh cages in fish farming. A prime verification of the biofouling resistance of copper-nickel and alloys came to light in 1987 when two early copper-nickel hulled vessels, the *ASPERIDA II* and the *COPPER MARINER*, were located after being in service for 21 and 16 years, respectively. Neither vessel required hull cleaning nor had suffered significant hull corrosion during that time.[7]

The 70-30 alloy is used in marine applications where its higher strength is an advantage; e.g., the seawater piping systems in deep diving submarines or often in fire protection systems. Its biofouling resistance is marginally less than that of the 90-10 copper-nickel composition. The 90-10 copper-nickel has the best combinations of corrosion, velocity induced erosion and biofouling resistance and is the preferred alloy for protection of marine structures. Due to its lower nickel content, the 90-10 alloy is of course less costly as well. The 70-30 copper-nickel is more costly, but has somewhat higher velocity induced erosion resistance than the 90-10 alloy. The 70-30 nickel-copper (Alloy 400) is much less resistant to fouling than the copper-nickels due to its lower copper content of 30%.

Sheathing and Offshore Structures

Experience with Ship Hulls

As noted above, the use of copper-nickel to provide a corrosion and biofouling resistant ship hull has been extensively utilized on scores of boats of a variety of hull constructions. The most publicized is the 22-m shrimp trawler *COPPER MARINER* built for the Nicaraguan Ministry of Fishing in 1971[7]. This boat has a 6 mm-thick 90-10 copper-nickel hull and is still in service. The hull has never required maintenance. Solid copper-nickel hulls are practical for boats on this order of size. In large oceangoing freighters or tankers where a corrosion and biofouling resistant hull would markedly improve fuel economics and reduce maintenance costs, some practical means of applying a relatively thin layer of copper-nickel to the steel hull is needed. *COPPER MARINER II* and a series of fire boats[11] were built using copper-nickel clad steel; i.e., a composite material having a metallurgical bond between the steel and copper-nickel alloy. These boats have been very successful, but the clad steel may be too expensive for widespread utilization. An alternative is to sheath the ship or structure. Sheathing refers to the attachment of relatively thin copper-nickel plate to the steel by welding, adhesives, or in the case of offshore jacket structure members, by mechanical methods such as clamping or screwing in place, often with an electrical insulation material between the steel and the copper-nickel. Examples of these methods are discussed below.

Offshore Structures

Both the fouling resistance and corrosion protection aspects of copper-nickel sheathing are critical to protecting offshore structures. The attachment and growth of marine organisms can add considerable weight to a structure; but more importantly, the increase in side loads on the structure due to currents, wind and waves is a major design consideration. Marine growth as thick as 0.7 to 1.2 m has been seen. Excessive marine growths extend frequently to about 1 m above mean sea level to about 10 meters below. Very large amounts of extra steel structure must be provided to resist the resulting forces. Regular and expensive removal of marine growth by divers using high pressure water is also required. As will be discussed below, sheathing can reduce these costs dramatically and provide overall savings to the platform owner.

Corrosion and Protection of Steel Structures in Sea Water. The intensity of corrosion of an unprotected steel structure in seawater varies markedly with position relative to the mean high and low tide level as shown in Figure 3.

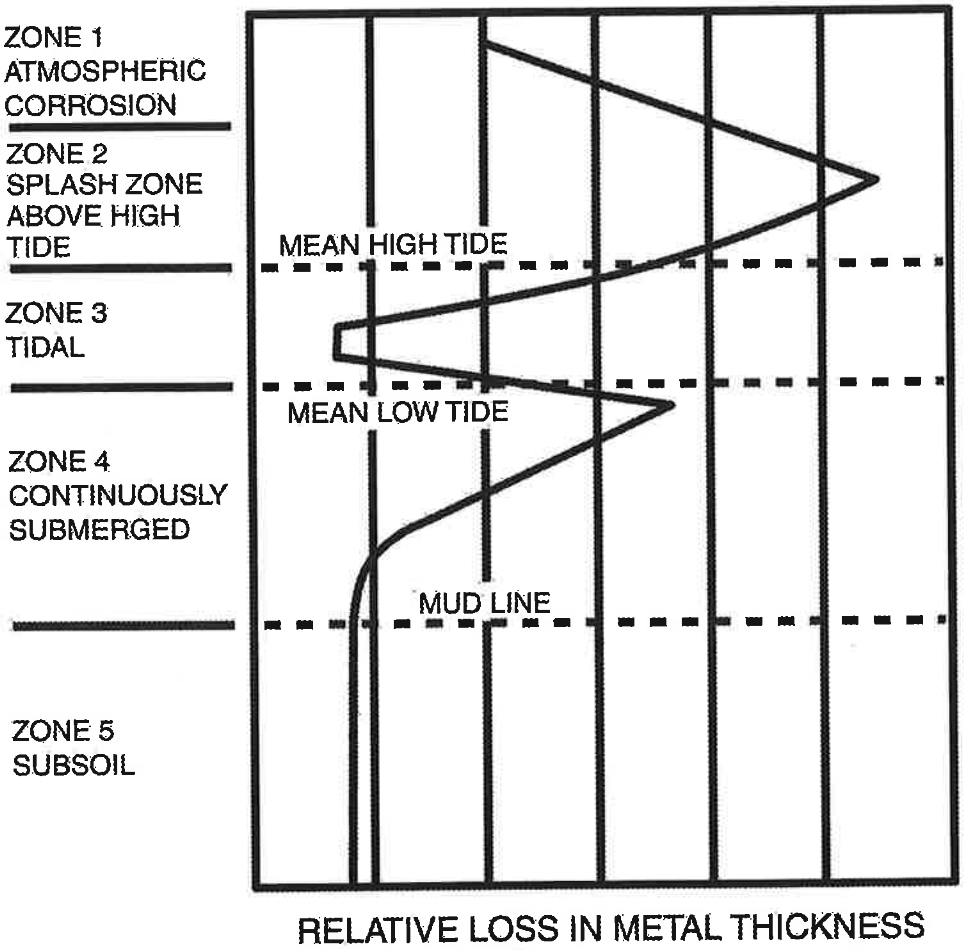

Figure 3 Profile of the Thickness Loss Resulting from Corrosion of an Unprotected Steel Structure in Seawater.

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/y at Cook Inlet, Alaska, and 1.4 mm/y in the Gulf of Mexico have been reported. Cathodic protection in this area is ineffective because of lack of continuous contact with the seawater, the electrolyte, and thus no current flows for much of the time. Corrosion rates of bare steel pilings are often also very high at a position just below mean low tide in a region that is very anodic relative to the tidal zone, due to powerful differential aeration cells which form in the well aerated tidal region.

Protection of a steel structure can be affected by various means; each corrosion zone must be separately considered. Three generally accepted methods are cathodic protection, painting or coating, and sheathing. Sheathing has proved to be a very successful approach when applied in the region through the splash/spray zone to a short distance below the tidal zone. As early as 1949, 70-30 nickel-copper (Alloy 400) was utilized on an offshore platform in the Gulf of Mexico off the Louisiana coast[12,13].

Early Sheathed Piling Trials. The LaQue Center 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. Sheathing or protective materials tested included 70-30 nickel-copper (Alloy 400), 18-8 chromium-nickel AISI Type 304 stainless steel, 70-30 copper-nickel, and both nickel (Nickel 200)-clad and 70-30 nickel-copper (Alloy 400) clad on steel. All of these were reported to be performing very well after 39 years of exposure.[14]

A large number of proprietary coatings, including galvanizing and sprayed zinc and aluminum, were also tested; all proved to have finite effective lifetimes extending up to 13 years[15]. The 90-10 copper-nickel alloy was not included in these early sheathing trials because its composition with regard to iron and manganese was not yet established.

Directly Welded Sheaths-Galvanic Effects. In the early trials, the 70-30 nickel-copper (Alloy 400) and the 70-30 copper-nickel alloy sheaths were welded directly to the steel. One might assume that corrosion of the anodic steel below the tidal zone would be accelerated because it is in direct contact with the more noble sheathing alloy. A number of experiments were conducted at the LaQue Center to investigate this possibility[14]. On the contrary, steel below the tidal zone is found to be cathodic relative to the noble alloy sheathing material, since the sheathing alloy, which is 70-30 nickel-copper (Alloy 400) in this case, becomes polarized to the potential of the adjacent steel below. Hence the submerged steel below the sheathed piling corrodes at a lower rate than the submerged steel on an unsheathed bare steel piling because the resulting galvanic current between the sheathed tidal zone and the submerged steel below it is lower.

This conclusion is confirmed by the results of galvanic corrosion tests conducted to determine the effects on submerged steel coupled to other alloys in the tidal zone[15], as shown in Figure 4.

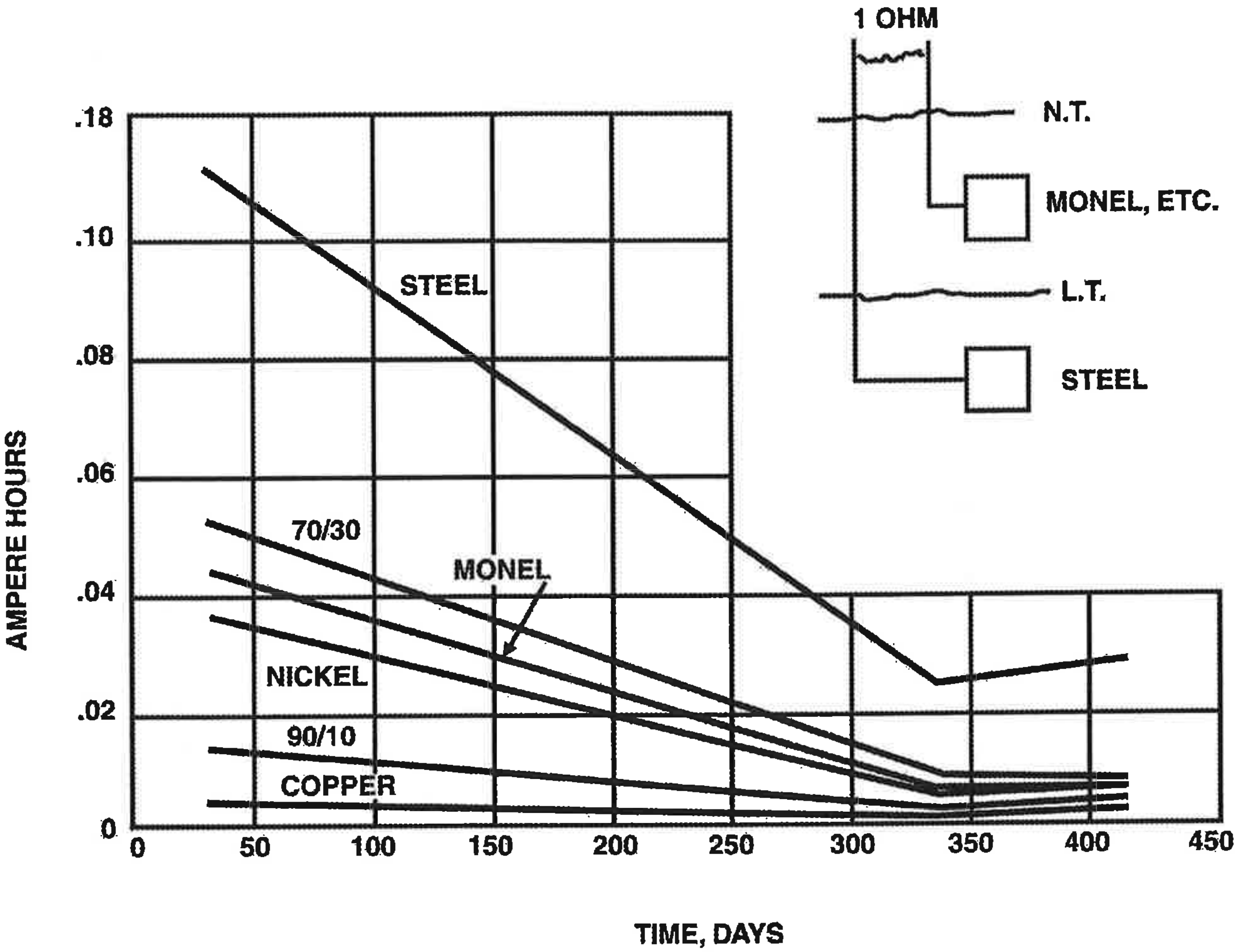

Figure 4 Total Current per Tide vs. Time between Plates in a Simulated Piling Test.

Plates of the alloys placed in the tidal zone are 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. Although the potential difference between the noble alloy-to-steel couples is significantly greater than the potential difference between two steel panels, the rapid and nearly complete polarization of the noble metal results in a lower galvanic current. More recently, the International Copper Research Association (now the International Copper Association) conducted several research programs clarifying and elaborating on these earlier findings[16,17,18]. In summary, steel under water corrodes less when in contact with noble metals in the tidal zone than when coupled to another panel of steel in the tidal zone.

As discussed above, the 90-10 copper-nickel alloy provides the best combination of corrosion resistance and biofouling protection. Attachment of this sheathing material to the steel structure by welding or mechanical fasteners will result in cathodic polarization of the sheath material and somewhat of a reduction in the antifouling capability of the 90-10 copper-nickel alloy. Therefore it is necessary to electrically insulate the sheath from the steel jacket members to gain the full advantage of the biofouling resistance properties of the alloy. Electrical insulation can be achieved by pumping cement or an epoxy into the annular space between the component and the sheath or, more simply, by use of an elastomer or rubber-base insulator. The copper-nickel can be in the form of sheet, wire grid, particles or flame-sprayed coatings. Bonding of the steel-elastomer-copper-nickel interfaces can be by vulcanizing, by the use of epoxy adhesives, by mechanical means or a combination of methods. Estimated costs of sheathing ranged from $194 to $322 per square meter ($18 to $30 per square foot).[19]

More Recent Sheathed Piling Tests. Long term exposure of copper-nickel sheathed steel pilings, to assess the effectiveness of corrosion and biofouling resistance as well as the cathodic protection systems in several configurations as described below was sponsored by the International Copper Association and the Copper Development Association Inc. and carried out at the LaQue Center in Wrightsville Beach, North Carolina. USA[20,21]. Over 50 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 piling 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.

The results of biofouling accumulations on these pilings are summarized in Table IV.

TABLE IV

BIOFOULING MASS ON 90-10 COPPER NICKEL SHEATHED STEEL PILINGS AFTER FIVE AND TEN YEARS

Piling	kg/m^2	Percent	Biofouling Organisms
Bare Steel*			
5 years	18.00	100.0	massive barnacles, oysters, etc.
10 years	12.00	100.0	
Concrete-Insulated Cu-Ni on Steel			
5 years	0.36	1.9	only scattered barnacles
10 years	0.14	1.2	
Cu-Ni Directly Welded to Steel			
5 years	7.95	44.3	moderate barnacles, oysters, etc.
10 years	4.43	36.8	
Rubber-Insulated Cu-Ni on Steel			
5 years	0.26	1.4	scattered barnacles, oysters, etc.
10 years**	0.51	4.2	
Rubber-Insulated Cu-Ni on Steel w/Galvanic Couple (single point contact)			
5 years	4.59	25.5	moderate barnacles, oysters, etc.
10 years***	15.39	37.0	

*	unsheathed - experimental control
**	average value (3 pilings)
***	average value (2 pilings)

Organisms observed include barnacles, oysters, codium, tunicate, colonial tunicate, encrusting and filamentious bryozoans but not all were present on all pilings, as shown in Table IV. After five years the mass accumulated on the bare steel piling was more than twice as great as that which accumulated on the directly welded 90-10 copper-nickel piling and more than 50 times higher than the average amount that attached to the concrete and rubber insulated sheathing. Only a few scattered barnacles were seen on the concrete insulated copper-nickel sheath after five years. After ten years the unsheathed bare steel is still heavily fouled but its fouling mass is somewhat reduced. However, the fouling mass of the rubber insulated pilings shows an increase over time while the concrete insulated pilings show a decrease when the five and ten year results are compared. The variability in fouling mass over time are normal, especially when one considers that this is a field test and therefore not conducted under controlled laboratory conditions. It is reasonable to assume that the two hurricanes that came ashore in the area in 1996 reduced the total accumulation of biofouling on heavily fouled pilings. All the sheathed pilings continue to resist fouling after ten years.

The galvanic anodes used on the cathodically protected piling were cleaned and weighed; mass loss and consumption rates are given in Table V.

TABLE V

GALVALUM III ANODE WEIGHT LOSS AND CONSUMPTION RATE WHEN COUPLED TO 90-10 COPPER-NICKEL SHEATHED STEEL PILINGS

Piling Type	Weight Loss* grams	Consumption Rate kg/yr
Bare Steel**		
2 years	716.4	0.36
5 years	1880.6	0.36
10 years	2316.1	0.23
Concrete-Insulated Cu-Ni on Steel		
2 years	755.3	0.38
5 years	1256.6	0.25
10 years	181.8	0.04
Cu-Ni Directly Welded to Steel		
2 years	414.1	0.21
5 years	687.6	0.14
10 years	2050.8	0.21

* combined weight - two anodes per piling
** unsheathed - experimental control

In the two-year exposures, the directly welded piling displayed a lower anode consumption rate than the bare steel; the concrete insulated consumption rate was comparable to that of the bare steel. After five years of exposure, both the directly welded and the concrete insulated pilings displayed reduced consumption rates. After ten years of exposure, the anode consumption rate of the directly welded copper-nickel on steel pilings returned to the rate initially observed after two years. This variability is also not unexpected when one considers that these are field exposures and are not conducted in a laboratory under controlled conditions. The reduction in anode consumption for the directly welded piling is considered to be due to the favorable polarization behavior of the 90-10 copper-nickel alloy. The reduced anode consumption rate for the concrete insulated piling is attributed to the high resistance path through the concrete to the underlying steel. The overall reduction in anode consumption rates for both sheathing techniques could in part be due to the reduction in current resulting from calcareous film formation on the 90-10 copper-nickel alloy.

It was also observed that even in the case where the sheathing is directly welded to the steel and exposed without cathodic protection for five years, there was no grossly accelerated attack of the steel immediately above or below the sheath. The average corrosion rates in the steel adjacent to the sheathing below the mean low tide point did not exceed 0.25 mm/y, which is no higher than the corrosion rate of the freely corroding, unsheathed steel control pilings. Of course, exposure of any steel piling without cathodic protection is not recommended.

A second series of experiments were conducted at Kure Beach, North Carolina, USA, at an oceanfront site by the LaQue Center[22]. A total of six pilings were exposed to oceanfront wave action, three on the north side and three on the south side of a fishing pier, slightly offshore from the wave breaker line. Their biofouling mass was measured after ten years and is shown in Table VI.

TABLE VI

BIOFOULING MASS ON 90-10 COPPER NICKEL SHEATHED STEEL PILINGS AFTER TEN YEARS OF EXPOSURE ON THE OCEANFRONT AT KURE BEACH, NORTH CAROLINA, USA

Piling	kg/m^2
Bare Steel (north side)*	3.61
Bare Steel (south side)*	2.92
Directly Welded on Steel (north side)	2.34
Directed Welded on Steel (south side)	2.34
Concrete Insulated Steel (north side)**	1.56
Concrete Insulated Steel (south side)	0.59

* unsheathed - experimental control
** partially shorted

As expected, the bare steel experiment controls had the highest biofouling mass, which was 500% to 600% greater than the value obtained from one of the concrete-insulated pilings (south side). The biofouling mass on the other concrete insulated piling (north side) was two-thirds the average amount accumulated on the directly welded piling. Note that the large accumulation on the concrete insulated piling (north side) was attributed to it being partially electrically shorted and therefore is more representative of a directly welded rather than insulated sheathing. The biofouling mass of the directly welded piling was 65% to 80% of the amount which grew on the bare steel experimental control pilings. However, the fouling on the latter copper-nickel-directly welded-to-steel pilings, was poorly adherent and easily removed.

Exxon Economic Analysis

The Exxon Production and Research Company carried out a generalized economic evaluation[23] for the International Copper Research Association by means of a computer aided design study of a conventional steel structure as depicted in Figure 5.

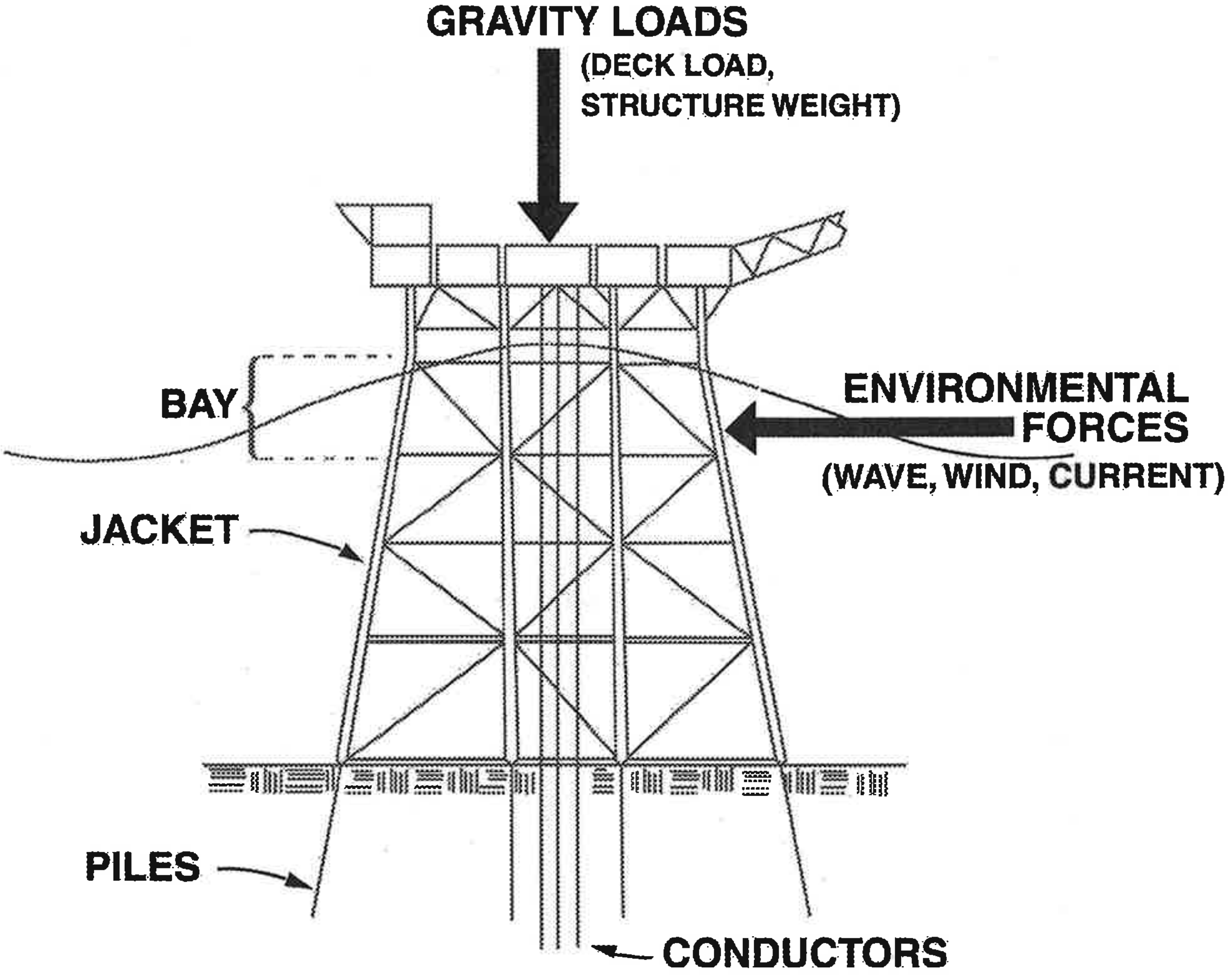

Figure 5 Simplified Diagram of Forces Acting on Off-shore Structures

Only insulated copper nickel alloy sheathing systems were considered as these gave the full economic benefits by minimizing of both marine fouling and corrosion. Design models were worked out for a range of situations, covering three different water depths, environmental conditions (wind, wave and current) ranging from mild to severe, and marine growth ranging from light to heavy. In all, 29 scenarios were considered. Potential cost savings were calculated based on the savings in weight of installed steel. The cost of the sheathing material and its installation were not included in the analysis, because of variability of the means of attachment and lack of data on these costs.

The gross savings for offshore structures per unit area of sheathing, which factors in all the total steel, fabrication and installation costs, are summarized in Figure 6.

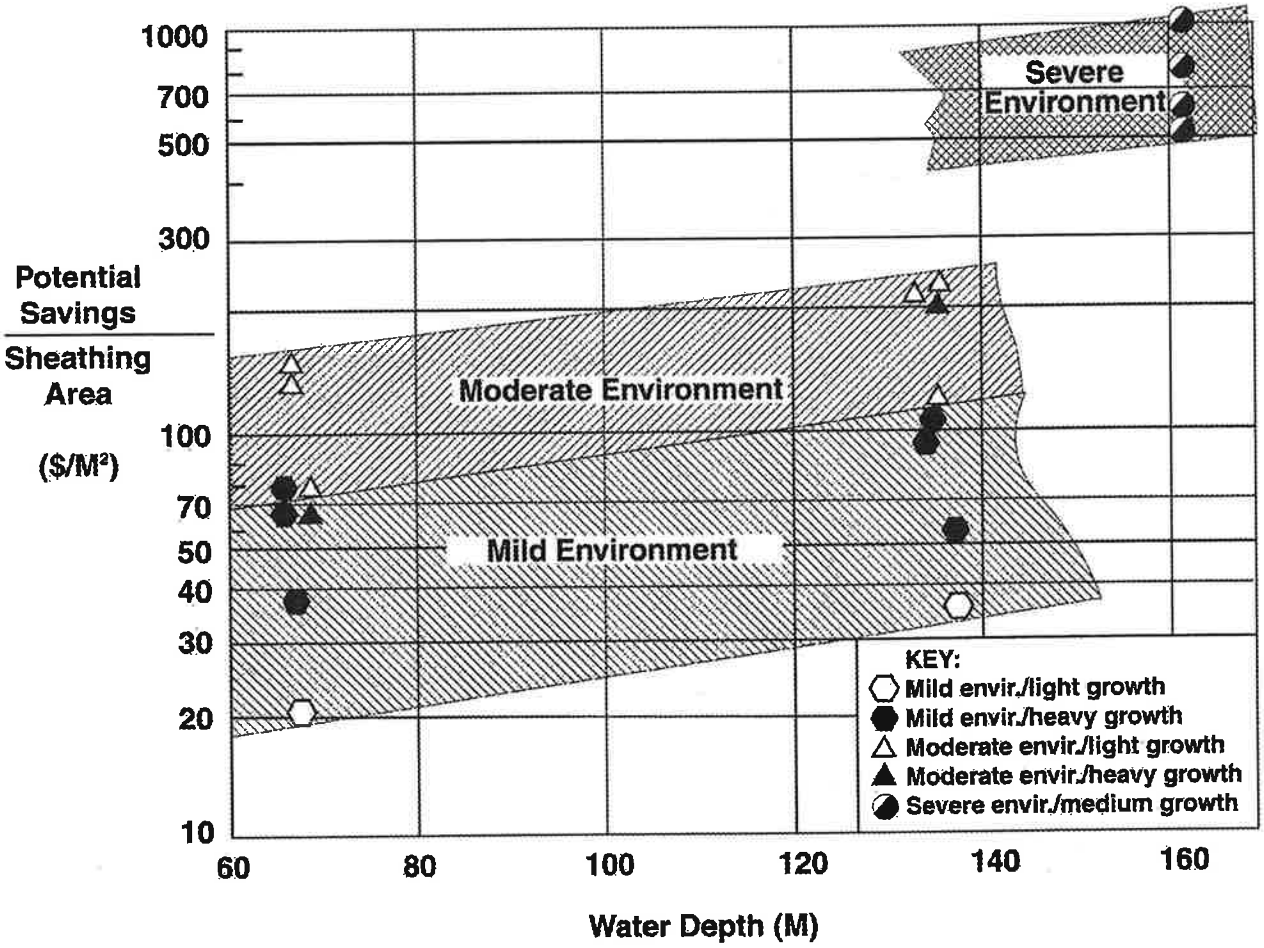

Figure 6 Potential Savings per Unit Area of Sheathing for Various Environments and Water Depths

In the mild environment, total weight savings, which is mostly attributable to reduction in steel, ranged from 9 tonnes up to 174 tonnes. For the various cases (depending on the depth of the water and the size and geometry of the off-shore structures), cost savings are up to a maximum of 5% of the total structure cost. In the moderate environment, weight savings ranged from 80 to 404 tons of steel and cost savings of 1.8% to 5.9% of total cost. The corresponding values for the severe environment were weight savings of 732 to 2372 tons of steel and 2.9% to 9.3% in cost savings.

Additional savings from reduced cleaning, maintenance and repair costs, again not included in the Exxon study, can be anticipated.

Field Experience - Sheathing Systems

British Gas Experience, Morecambe Bay, UK. The structures deployed in Stage One of the Morecambe Field project were sheathed with 90-10 copper-nickel alloy by welding 4 mm thick plate directly to the steel legs over the tidal and splash zones from 2 m below low tide level to 13 m above. A production platform, an accommodation platform, three drill platforms and a flare stack have been so treated. The main purpose of the sheathing was to provide corrosion protection in the splash zone. The submerged portion of the structure was protected by zinc anodes, which were directly attached to the steel. An economic assessment[24] indicated that the 90-10 copper-nickel alloy sheathing was more cost effective than either the 70-30 nickel-copper (Alloy 400) sheathing or conventional systems using non-metallic coatings, which necessitate increasing the thickness of the steel because of the mandated corrosion allowance for structures.

The certifying authorities required a sacrificial steel corrosion allowance (12 mm thickness) in this highly corrosive area when a paint system or neoprene wrap is specified. A sacrificial steel corrosion allowance is not required with the copper-nickel or nickel-copper (Alloy 400) metal wrap system. The economic justification was based on a platform life of 15 years. All maintenance costs were discounted to net present value at 10%. The costs associated with the painted, neoprene, and alloy sheathing approaches to protection against corrosion are summarized in Table VII

TABLE VII

ANALYSIS OF SYSTEM COSTS FOR SEVERAL COATINGS
OR SHEATHINGS FOR SPLASH ZONE PROTECTION
System Costs, Million Pounds Sterling

	Protective Coating/Sheathing			
	Paint	Neoprene	Alloy 400	90-10 Cu-Ni
Initial Cost - Extra Steel	2.3	2.3	-	-
Protective Material & Labor	0.1	0.3	2.2	0.95
Maintenance Cost	2.4(1)	unknown(2)	0.15(3)	0.15(3)
Extra Weight (tonnes)	660	660	180	180

---

(1) Repainting 8 years after installation and every 5 years thereafter

(2) No long-time experience; no large scale repairs assumed in less than 18 years

(3) Minimum maintenance, confined mainly to accident repair

and shown, on a relative cost basis, in Figure 7.

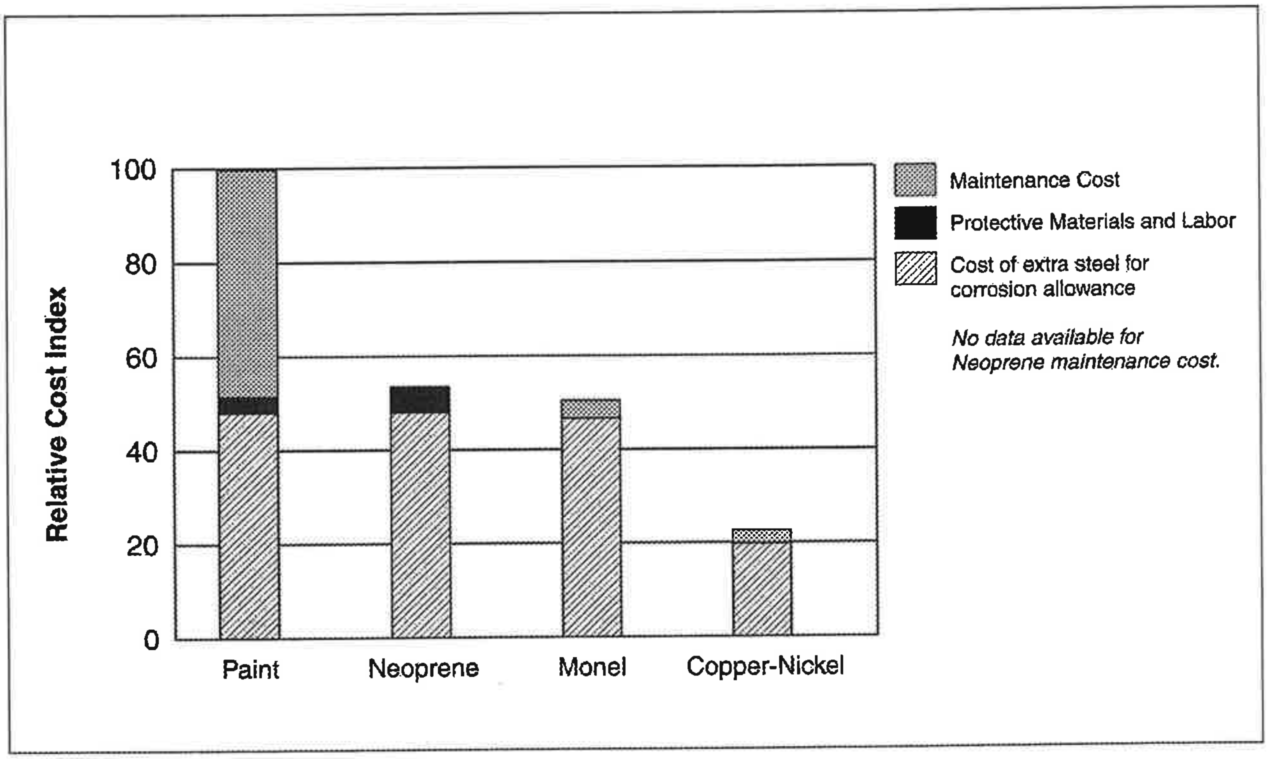

Figure 7 Relative System Costs for Protective Sheathing

The advantages of 70-30 nickel-copper (Alloy 400), and even to a greater extent, copper-nickel sheathing are apparent. For life spans in excess of 15 years, the costs savings and advantages of using the metallic sheathing systems, especially the highly fouling resistant 90-10 copper-nickel, will be even greater.

The Morecambe Field jackets have been inspected at intervals since initiation of service in 1985. Underwater video records of the condition of the steel and sheathed splash zone regions are available. These show that there is no significant corrosion of the steel or copper-nickel sheath. As a precautionary measure, the amount of cathodic protection applied was increased significantly by applying some 500 zinc anodes. With the heavy cathodic protection, there is some marine fouling on the copper-nickel since it is welded directly to the steel, but this fouling is very 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.

Shell Beta Site - California. A proprietary system called "Bio-Shield" developed by the Shell Development Company, has met with considerable success on offshore installations off the coast of California[25]. Biofouling can be quite severe along the southern California coastline with three-year marine growth exceeding 200 mm immediately above to about 12 m below mean sea level. To ensure optimum effectiveness of the copper-nickel, an insulated system was selected. Bio-Shield consists of 1.6-mm thick 90-10 copper-nickel sheet and a high-density 12.5 mm thick elastomer, with the trade name of Splashtron made by the Mark Tool Company of Lafayette, Louisiana. After a laboratory test program, this system was applied to the design of the 214-m water depth Eureka platform with 60 well conductors (0.6 m OD). A total of 152 tonnes of structural steel, otherwise required to handle the extra wave, tide and current loading from the marine growth, was eliminated. The platform was installed in July 1984. After several years, the copper-nickel surface of the Bio-Shield was free of fouling while the unprotected areas were covered with an 8 to 13 cm thick layer of barnacle and mussel growth. This attests to the effectiveness of a fully electrically insulated copper-nickel sheath. Platform response values were reduced as follows: wave forces, -6%; base shear -10%; overturning moment, -10%; deck deflection, -10%; and pile load, -7%. A reduction in platform response values directly translates into cost benefits. Reducing marine growth can clearly reduce platform costs. Money was saved in reduced steel for corrosion allowance and lower fatigue loads in the major platform joints (structural nodes). Estimated savings realized from installing the sheathing system on the 60 conductors from 1.5 m above mean low water line to 4.9 m below mean low tide for the 214 m structure are presented in Table VIII.

TABLE VIII

ESTIMATES OF COST SAVINGS FOR OFFSHORE INSTALLATIONS BY USING A 90-10 COPPER-NICKEL INSULATED SHEATHING SYSTEM

Conductors - 55 tons x $1000/ton	=	$ 55,000
Paint - 10,600 ft.^{2} x $3/ft^2	=	32,000
Anodes - $1250 each x 4	=	5,000
Structural Nodes - 114 tons x $2500/ton	=	285,000
Total	=	$377,000

Savings per cleaning were also estimated at $50,000 to $100,000. Installed costs for this system on the Eureka platform were reported to be $250,000 or about $340/m^2 ($31.60/ft^2). Clearly, this installation of a copper-nickel sheath system was very cost effective.

Service Experience of 70-30 Nickel-Copper (Alloy 400). Field experience for 70-30 nickel-copper (Alloy 400) splash zone protection of legs dates back 50 years and for 30 years for risers.

In 1949, 70-30 nickel-copper (Alloy 400) was first used in the Gulf of Mexico, three miles from the Louisiana coast. Three materials, 70-30 nickel-copper (Alloy 400), 70-30 nickel-copper (Alloy 400) clad on steel and unalloyed nickel (Nickel 200) 1.5 mm welded sheathing were examined. All survived after more than five years of battering by boats. In conclusion, all were satisfactory but 70-30 nickel-copper (Alloy 400) was considered the most economic choice. The 90-10 copper-nickel alloy had not been fully defined at the time of this work and was not included.

Aramco first used 70-30 nickel-copper (Alloy 400) in the Arabian Gulf for legs and risers in the late 1950s, as reported by Hopkins.[26]

BP experienced splash zone corrosion in 1967 in the Middle East. Prior to that, risers were coated with coal tar epoxy, then clad with concrete. A concrete coating on a riser was damaged in Umm Shaif field due to a boat collision and the coal tar peeled off under gravity. In six months the riser wall was corroded through. Oil escaped and ignited burning down the entire platform. BP then put 70-30 nickel-copper (Alloy 400) sheathing on 49 risers in the Gulf at 3mm thickness. BP continued this practice when they began operations in the Forties Field in the North Sea in 1974. This has continued to the present day although neoprene is also now being used.

Phillips started to use 70-30 nickel-copper (Alloy 400) on risers following an explosion on 2-4 Alpha platform in Ekofish in 1975. Again a concrete coated riser 10 in dia. was damaged but the underlying bitumen was still intact. Severe crevice corrosion occurred and corroded 7 mm of the 10 mm thick wall in two months at 90C. The riser carrying gas fractured resulting in a massive escape of oil and gas. Phillips took action to remove all the remaining risers, and sheathed them with 5 mm thick 70-30 nickel-copper (Alloy 400) over a 25-m height span.

In 1979, at salty Lake Maracaibo in Venezuela, a riser externally coated with neoprene rubber failed due to poor application and embrittlement after four years service at 100C. A spiral defect allowed the water to reach the surface, resulting in crevice corrosion and 7 mm in corrosion penetration, which subsequently led to an explosion. Again 70-30 nickel-copper (Alloy 400) was introduced for temperatures greater than 70C.

The feedback about the performance of 70-30 nickel-copper (Alloy 400) in splash zone applications over the last 50 years has been excellent. 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 failures occurred in BP 20 in risers on Forties field. A cofferdam was put around the risers to facilitate removal. The divers noted a pressure release when they removed the sheathing and hydrogen gas was detected. Destructive testing failed to find any evidence of hydrogen embrittlement. 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. The pressure was 2000 to 3000 kilopascals (KPa). 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. Hydrogen diffused through the riser causing a pressure buildup, and it was at such a high level that it caused mechanical damage of the sheathing. Holes were drilled in the top of the sheathing to relieve the pressure in the interim and measures were taken to ensure adequate inhibition in the longer term.

Several projects in S.E. Asia have recently selected 70-30 nickel-copper (Alloy 400) metallurgically clad pipe for hot risers as shown in Table IX.

TABLE IX

S.E. ASIA PROJECTS UTILIZING 70-30 NICKEL-COPPER (ALLOY 400) CLAD PIPE FOR HOT RISERS

Company	Project	Materials	Diameter	Thickness	Length	Tonnage
Sarawak Shell Burhad	MLNG DUA II	API X52 plus Alloy 400 cladding	998mm	35.75 mm	70 m	60
Sarawak Shell Burhad	Bardegg	API X60 plus ASTM B127 UNS N04400	10 in 12 in 18.5 in	9.6 + 3 mm 9.6 + 3 mm 9.6 + 3 mm	18.3 m 18.3 m 18.3 m	11
Esso Production Malaysia Inc.	Gud and Lawit JEA07 and TAP 35 projects	API X65 plus ASTM B127 UNS N04400		9.6 +4 mm 12.7+ 4 mm	15.8 m 13.9 m	6
Esso Production Malaysia Inc.	Lawit A	API X65 plus ASTM B127 UNS N04400	30 in.	28 + 4 mm	14.3 m	9
Esso Production Malaysia Inc.	Seligi D to C	API X65 plus ASTM B127 UNS N04400	6 in.	9.6 + 4 mm	16 m	2
Sarawak Shell Burhad	Kinabalu	API X60 plus ASTM B127 UNS N04400	8 in 12 in 14 in	9.5 + 2 mm 9.5 + 2 mm 9.5 + 2 mm	12.2 m 12.2 m 12.2 m	7
Esso Production Malaysia Inc.	Tapis	API X65 plus ASTM B127 UNS N04400	24 in	22.2+ 2.5 mm	12 m	5

Limited Field Experience with 18-8 Chromium-Nickel Type 304 Stainless Steel. In 1958, two pilings were sheathed with a six-foot band of 18-8 stainless steel, which extended from above the splash zone to below the tidal zone, and driven into the mud at the wharf at the LaQue Center, Wrightsville Beach, North Carolina, USA. On one piling, the sheathing was welded at the top and bottom as well as at the overlap seam to exclude air and seawater. On the second piling, the sheathing was attached with stainless steel machine screws, but neither the top nor bottom was welded to the piling. Kirk[14] reported that the sheathing was in good shape on both pilings after 28 years of exposure, as did Kain[27] after 34 years. It is known that sacrificial zinc anodes, which were attached to the steel below the sheathing provided some cathodic protection through the mid-1980s, when this practice was discontinued. After 40 years[28] the bare steel exposed below the mud-line was near its original condition and the raised features of the welds were clearly seen. Furthermore, the steel beneath the sheathing was fully protected in both the splash and spray, and tidal zones. One thorough-wall penetration of the steel piling below the lower end of the weld sheath, which is below the waterline, was observed. In addition, local corrosion ranging or penetrations from 3.6 to 2.5 mm in depth were seen on both pilings.

The extent to which these penetrations were attributed to either self-corrosion or galvanic attack could not be determined. Stainless steel offers no biofouling resistance. The use of stainless steel should be limited to ambient temperature to avoid stress corrosion cracking. Therefore it is not an appropriate material for sheathing hot risers. However, the combination of stainless sheathing on steel pilings can be used when sacrificial zinc anodes are provided and fouling is not deemed a large issue.

Other Sheathing & Coating Systems

Zinc Clad Hydraulic Tubing. As an alternative to deep water oil platforms is to set the wellhead on the seabed and control their operation remotely with hydraulic lines. Southwestern Pipe of Houston, Texas, in cooperation with Shell Oil explored the possibility of using carbon steel wrapped in a zinc cladding to protect these hydraulic lines. A product, commercialized under the trademark SeaCAT, which consists of a 750-micron thick co-extruded zinc cladding on steel, was specified by Shell for two development projects in the Gulf of Mexico.

Thermal-Sprayed Copper-Nickel. A study conducted by Perkins and Marsh[29] at Lockheed in California demonstrated that it is technically feasible to arc-spray offshore structures with either copper or 90-10 copper-nickel. The process can be used to sheath complex shapes including nodes and welds that cannot be sheathed readily with sheet material. Free standing forms of either copper or 90-10 copper-nickel that replicate a contoured surface can also be arc-sprayed. Both arc-sprayed copper and 90-10 copper-nickel exhibited parabolic corrosion kinetics in seawater and both showed good resistance to biofouling during a 413-day exposure in San Diego harbor. These initial results show promise but additional experience is needed. Most importantly, the arc-sprayed coating allow non-destructive inspection of the underlying steel for fatigue cracks.

Adhesive Bonded Copper-Nickel. An adhesively bonded copper-nickel system known by the trade name *MITCHELL MARINER 706* has been used extensively in the sheathing of pleasure boats[30]. Wood, GRP and steel hulls have been so treated. There is no experience to date with this system on offshore structures, but it should be equally applicable there. *MITCHELL MARINER 706* consists of a 90-10 copper-nickel (C70600) foil, 0.15 to 0.25 mm in thick, where the thickness used depends upon on the intended application. The foil is coated on one side with a thick (~0.4 mm) mastic protected with a strippable backing paper. Thicker mastic layers are used for special purposes such as applying to old and pitted steel substrate after cleaning. This mastic has high electrical resistivity and very effectively insulates the copper-nickel from the steel ship hull or jacket member. It also allows some movement between the sheath and the steel and accommodates differences in thermal expansion characteristics. The mastic-coated foil is applied to the steel or other substrate with heat and some pressure. Gulf Ferries Ltd. of Auckland, New Zealand, sheathed two small ferries, both with GRP hulls, in this system in 1994.

Copper-Nickel/Resin Composite Systems

An antifouling undersea marker or identification system for pipelines, known as SEAMARK, is another interesting application of biofouling resistance of copper-nickel.[31] The markers achieve antifouling resistance from a surface layer of fine interwoven 90-10 copper-nickel wire mesh imbedded in a yellow pigmented polyester gel. The copper-nickel mesh is insulated from the steel substrate by an appropriate backing of fiberglass, polyurethane or rubber. The markers can be adhesively bonded, vulcanized, strapped, bolted or clipped in place. The mesh is typically 0.375-mm diameter wire and is flattened and embedded in the gel. To expose the copper-nickel to the seawater, the outer surface of the composite is abraded. A minimum of 22% surface cover is required for the copper-nickel to provide adequate antifouling properties. In 1993, more than 2000 of these types of markers were sold, mostly in the Norwegian sector of the North Sea.

Another approach to providing biofouling resistance[32,33] uses 1mm lengths of up to 1mm diameter chopped copper-nickel wire, which is embedded in neoprene. This product, Avonclad, has now been used for more than a decade. It consists of a mono-layer of copper-nickel chopped wire embedded in and bonded to a 3mm neoprene sheet. The chopped wire is uniformly distributed over the surface to give a copper-nickel exposure area in excess of 30%. This composite can then be either hot bonded onto an elastomeric corrosion coating or cold bonded directly onto the steel piling.

Finally, a new coating system comprised of a copper-nickel alloy applied by thermal spray to a high solid epoxy coating has been developed for antifouling application. The process, known as COPPERLOK, is applicable to fiberglass, concrete, wood and steel[32]. In the case of steel surface, the bond coat provides the necessary dielectric insulation. Good adhesion of the thermally sprayed copper is achieved by implanted hollow microspheres in the resin bond coat. These are fractured to create anchor sites for the 90-10 copper-nickel alloy.

Summary

The properties of the copper-nickel and nickel-copper alloys are reviewed. The 90-10 copper-nickel alloy is shown to have the optimum combination of corrosion and biofouling resistance. Sheathing of ship hulls with 90-10 copper-nickel is briefly reviewed, leading to the application of sheathing for corrosion and biofouling protection of offshore structures in the spray/splash zone. Trials of sheathed pilings and various attachment methods are reviewed. Sheathing of offshore structures results in reduced side forces due to tides, wind and waves. It is discussed how this translates into reductions in steel thickness and thus total jacket weight. Examples of the successful use of copper-nickel sheathing on offshore platforms and the 70-30 nickel-copper (Alloy 400) on risers are presented. Finally, several alternative sheathing systems including adhesively -bonded copper-nickel sheet and particulate copper or copper-nickel in resin matrixes are briefly introduced.

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