Technical Report

COPPER • BRASS • BRONZE

The Application of Copper-Nickel Alloys in Marine Systems

Copper Development Association Inc.

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The Application of Copper-Nickel Alloys in Marine Systems

Presented jointly by

International Copper Association, Ltd.
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Copper Development Association Inc.

MARINE APPLICATIONS OF COPPER-NICKEL ALLOYS

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Mr. Kirk recently retired as president of the LaQue Center for Corrosion Technology after 30 years of service devoted to the testing and evaluation of materials - particularly copper-based alloys, steels, stainless steels and nickel-base alloys - in marine environments. He managed the Center for 23 years, prior to which he was supervisor of research. He had spent four previous years with the Westinghouse Bettis Atomic Power Laboratory where he was co-developer of Zircaloy-4.

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Mr. Todd studied metallurgy at Liverpool University and graduated with a Bachelor of Engineering degree (First Honors) in 1948. He worked for the Ocean Group of Shipping Companies as chief metallurgist until 1965 when he joined INCO Europe Market Development Department as manager of marine industries. In 1980 he became managing director of INCO Middle East Projects and worked as a consultant on materials and corrosion to several Middle Eastern organizations, notably the Saline Water Conversion Corporation, Saudi Arabia, and the Ministry of Electricity and Water, Qatar.

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DALE T. PETERS

Dr. Peters is vice president, technical and environmental, at the Copper Development Association Inc. (CDA) where he directs a broad range of programs to promote the use of copper and copper alloys and to identify new markets.

Before joining CDA, he was technical director of the Metallurgy Program of the International Copper Association, Ltd. in New York. Prior to coming to the copper industry, Dr. Peters held a number of positions in product research and development at the INCO Ltd. laboratory, Sterling Forest, New York, including management of laboratory service functions in chemical analysis, metallography, and electron beam instrumentation. He initiated INCO research activity in magnetic materials and advanced secondary batteries and manufacturing technology.

Dr. Peters received his B.S. in Metallurgical Engineering at the University of Cincinnati and his Ph.D. in Metallurgy from The Ohio State University in Columbus, Ohio. He received an award as a Distinguished Alumnus of the University of Cincinnati in 1985. He has authored or coauthored more than 30 technical papers and holds several U.S. and foreign patents.

Dr. Peters is a member of a number of technical societies including ASM International, TMS, American Foundrymen's Society, Materials Research Society, SAE, ASME, and the National Association of Corrosion Engineers.

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Mr. Avery has extensive experience in welding technology gained first at Bethlehem Steel Shipbuilding Division in Quincy, Massachusetts, and subsequently at INCO Alloys International, Huntington, West Virginia. At Bethlehem, Dick Avery was the welding engineer on the USS Bainbridge nuclear destroyer. At INCO Alloys International, he was in Technical Service, Market Development and Marketing.

He now serves as a consultant to the Nickel Development Institute and other clients as Avery Consulting Associations Inc. His specialties besides welding including metallurgy and corrosion of stainless steel, nickel alloys and the copper-nickel alloys. He obtained his BS in Metallurgical Engineering from Rensselaer Polytechnic Institute.

COPPER-NICKEL ALLOYS – RESISTANCE TO CORROSION AND BIOFOULING

C.A. POWELL, Consultant, Nickel Development Institute

INTRODUCTION

The attractive corrosion- and biofouling-resistance of copper-nickel alloys in seawater and related environments have led to their substantial use in marine service for many years. This introduction, will review the properties of the more commonly encountered alloys, while subsequent papers will detail some of their applications.

Historical

The two main, wrought copper-nickel alloys chosen for seawater service contain 10% or 30% nickel, respectively. Both have important additions of iron and manganese which are necessary to maintain good corrosion resistance. Their development was based upon the understanding of how these additions, particularly iron, influence the alloys' properties.

Development work began in the 1930s in response to a requirement by the British Navy for an improved condenser material. The 70-30 brass used at that time could not adequately withstand prevailing seawater velocities. Based on observations that the properties of 70-30 copper-nickel tended to vary with iron and manganese levels, a composition was sought to optimize resistance to velocity effects, deposit attack and pitting corrosion. Typical levels of 0.6% iron and 1.0% manganese were finally chosen.(1)

Once successful service experience was achieved, interest was transferred to lower nickel compositions, initially as a replacement for copper seawater pipe work in naval applications. The 10% nickel alloy was eventually chosen, although in this case the optimum composition was identified to have a higher iron content and lower manganese level than the 70-30 alloy at typically 1.5% and 0.8%, respectively.

Since the 1950s, the 90-10 alloy has become accepted for condenser service as well as for seawater pipe work in merchant and naval service. In naval vessels, the 90-10 copper-nickel is preferred for surface ships; whereas, the 70-30 alloy is used for submarines because its greater strength makes it more acceptable for the higher pressures encountered. These alloys are also used for power station condensers and offshore seawater pipe work on oil/gas platforms. Large quantities are selected for the desalination industry and they are additionally used for cladding and sheathing of marine structures and hulls.

Composition

When comparing international specifications, the compositional ranges of the two alloys vary slightly from specification to specification as can be seen in **Table 1**. In practice, these variations have little influence on the overall service performance of the alloys.

Iron is essential for both alloys because it provides added resistance to corrosion caused by velocity effects called impingement attack. **Figure 1** shows the effect of iron content on the impingement attack on 90-10 copper-nickel from 30-day tests obtained at 3 m/s water velocity.(2) This is taken from the data compiled by various authors and different test facilities. A distinct minimum is apparent between 1.5 and 2.5% iron. Optimum iron levels are a result of solid solubility. The corrosion resistance improves with increasing iron so long as it remains in solid solution. The specification limits for alloys were set by this observation.

Other properties also require consideration, and **Figure 2** shows a schematic presentation by Gilbert(3) and of the iron compositional balance sought in the 90-10 and 70-30 alloys to optimize impingement resistance and resistance to various forms of localized corrosion.

Manganese is necessary as a deoxidant during the melting process, but its effect on corrosion resistance is less well defined than iron's. At lower levels of iron content, however, higher manganese levels lead to improved impingement properties.

Impurity levels must be tightly controlled because elements such as lead, sulphur, carbon and phosphorus, while having minimal effect on corrosion resistance, can influence hot ductility and, therefore, influence weldability and hot workability. Reputable suppliers are aware of this and endeavor to manufacture material with restricted impurity levels well within the specifications.

TABLE 1

Comparison between various specifications for 90-10 and 70-30 Copper Nickel Alloys.

(Maxima except where range given)

90-10

	ISO	BS	ASTM	DIN
	CuNi10Fe1Mn	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
	CuNi30Mn1Fe	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.

TABLE 2

TYPICAL MECHANICAL PROPERTIES OF 90-10 AND 70-30 COPPER NICKELS

Property	90-10	70-30
Proof Stress N/mm²	140	170
Tensile Strength N/mm²	320	420
Elongation, %	40	42

Mechanical Properties

Typical annealed mechanical properties for the two copper-nickel alloys are shown in **Table 2**. Both alloys have good mechanical strengths and ductilities, although the higher nickel alloy does possess the greater inherent strength. Both alloys are single phase, solid solution alloys and cannot be hardened by heat treatment. The strengths, however, can be increased by work hardening. Whereas, 90-10 copper nickel tubing can have a proof stress of 100-160 N/mm² when supplied in the annealed condition, this could typically be 345-485 N/mm² in the as-drawn condition.

Physical Properties

A comparison of the physical properties of the two alloys are given in **Table 3.**[4] Of particular interest for heat exchangers and condensers are the thermal conductivity and expansion characteristics. Although conductivity values for both are good, the 90-10 alloy has the higher value. This partly explains the alloy's greater popularity for heat exchanger and condenser service, where higher strength is not the most important factor.

The 70-30 alloy is essentially nonmagnetic and has a magnetic permeability very close to unity. The 90-10 alloy with higher iron content is nonmagnetic, if the iron can be retained in solid solution during processing. For 90-10 tubing used in minesweepers, air cooling after the final anneal suppresses precipitation sufficiently to provide low permeability.

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 seawater has confirmed its good resistance to the wide range of corrosion mechanisms.

TABLE 3

Physical Properties.

Property	90-10	70-30
Specific Gravity g cm^{-3}	8.9	8.95
Specific Heat J/kg K	377	377
Melting Range °C	1100-1145	1170-1240
Thermal conductivity W/mK	50	29
Coefficient of linear expansion.		
-180 to 10C 10^{-6} K	13	[illegible]
10 to 300C 10^{-6} K	17	[illegible]
Electrical Resistivity microhm cm	19	34
Coefficient of electrical resistivity 10^{-5} K	70	50
Modulus of Elasticity GN/m^{2}		
annealed	135	152
cold worked 50 per cent	127	143
Modulus of Rigidity GN/m^{2}		
annealed	50	56
cold worked	47	53

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(5) 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(6) in quiet, flowing (0.6 m/s) and tidal conditions are shown in Figures 3 and 4. It was found that, in all instances, corrosion rates were higher during early stages of testing, before stabilizing at lower values. 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 was true for quiet as well as flowing conditions, but corrosion rates were consistently lower for tidal conditions throughout. Both alloys show low general corrosion rates, with the 70-30 alloy having slightly better overall levels.

Pitting and Crevice Corrosion

Alloys protected by a passive film, such as stainless steels, tend to have low general corrosion rates but can suffer localized corrosion once the film is 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.

Although copper-nickels have a passive surface film, they have advantages over some other alloy types by having a high resistance to biofouling, thereby decreasing the number of potential sites where corrosion could occur. The copper-nickels also have a high inherent resistance to pitting and crevice corrosion in quiet seawater. Pitting penetration rates can conservatively be expected to be well below 0.127 mm/year. Sixteen-year tests(7) on 70-30 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 undercut 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.(2) When encountered, it tends to be metal ion concentration cell corrosion – the opposite of that occurring in stainless steels, for example. Metal ions accumulate in the crevice area and the crevice becomes noble. Dissolution occurs adjacent to the crevice on surfaces exposed to oxygenated bulk seawater. Water velocity can aggravate this type of attack, although penetration rates are unlikely to be severe.

Stress Corrosion Cracking

The 90-10 and 70-30 copper-nickels are resistant to chloride- and sulphide-stress corrosion cracking.

Some copper-based alloys such as aluminum brass are subject to stress corrosion cracking in the presence of ammonia. In practice, this prevents their use in the air-removal section of power plant condensers. Copper-nickel alloys, however, are resistant to stress corrosion cracking and are commonly used in air-removal sections.

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 alloy is slightly more noble than the 90-10 alloy but not significantly so. The two alloys, therefore, can successfully be coupled.

Weld Areas and Denickelification

The corrosion resistance of weld deposits made by approved weld consumables and of the adjacent, heat affected zone in these alloys does not pose a problem, as may be the case in some other alloy systems. The 90-10 alloy is normally welded with a 70-30 copper-nickel consumable and provides a weld which is galvanically slightly more noble than the base metal. Nickel-copper (65Ni-35Cu) consumables are used for copper-nickel to steel welds.

Denickelification in the 70-30 alloy has been encountered occasionally in refinery overhead condenser service, where hydrocarbon streams condense at temperatures above 150 C. This appears to be due to thermogalvanic effects resulting from the occurrence of local hot spots. The solution has been to remove deposits which lead to the hot spots, either by more frequent cleaning or by increasing flow rates.

PROTECTIVE FILM FORMATION

The good corrosion resistance in seawater offered by copper-nickel alloys results from the formation of a protective oxide film on the metal surface. The film forms naturally and quickly following the alloys' initial exposure to seawater.

In clean seawater, the film is predominantly cuprous oxide, with the protective value enhanced by the presence of nickel and iron. Cuprous hydroxy-chloride and cupric oxide are often also present.(7,8)

The film can be brown, greenish-brown or brownish-black. In 90-10 copper-nickel, the film thickness can be on the order of 4,400 A.(2,8)

The rate of film formation was portrayed by Tuthill(8) from measurements of the copper content of condenser seawater effluent over a three-month period after start up, **Figure 5**. Copper content was found to decrease to 1/10 in ten minutes and to 1/100 in an hour. After three months, the copper in the effluent was at virtually the same level as that in the intake water. This indirectly shows that the maturity of the protective film reduced the corrosion rate of the condenser 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 timespan approaches four years before the decrease in corrosion rate becomes negligible. In flowing water, the corrosion rate, as shown in **Figures 3** and 4, was found to decrease continually over at least a 14-year period, the effect being similar for both 90-10 and 70-30 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 sulphides present can interfere with film formation, producing a black film containing cuprous oxide and sulphide.(2) This film is not as protective and adherent as films formed in unpolluted water. However, if an established cuprous oxide film is present, then periodic exposure to polluted water can be tolerated without damage to the 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 protective surface film on the alloys. However, once the velocity is such that the film becomes damaged and the active underlying metal is exposed, erosion corrosion (impingement attack) will occur rapidly. The seawater velocity at which this occurs is often called the "breakaway velocity" and different copper-based alloys show different breakaway velocities.

Figure 6, prepared by Gilbert,(9) can be used to illustrate the relative velocity limitations for various copper-based alloys. The 90-10 copper-nickel has better impingement resistance than aluminum brass, which in turn is better than copper. The 70-30 alloy shows better resistance than the 90-10 alloy.

This is not a complete representation, however. Rates of attack are not only dependent on seawater velocity but also on pipe work diameter.

Many studies have evaluated the impingement resistance for marine condensers and piping involving several types of test apparatus, including rotating discs, rotating spindles, model condensers, multi-velocity jet tests and jet impingement tests. These trials have proved reliable in ranking materials as a function of impingement resistance, but results vary from one test apparatus and laboratory to another.

Table 4 compares results of tests on condenser tube alloys using the jet impingement technique in two laboratories; one in the UK and the second in the USA. These tests involve a jet of seawater containing 3% air, projected at about 5 m/s against a metal surface and then taking measurements of the depth of attack. Alloys with high resistance to impingement attack, such as iron-containing copper-nickel, show less penetration in this test than alloys of lower resistance. However, in this work it is notable that once-through natural seawater at the USA laboratory caused

TABLE 4

COMPARISON OF THE RESULTS OF TESTS ON CONDENSER TUBE ALLOYS IN THE BRITISH NON FERROUS METAL RESEARCH ASSOCIATION LABORATORIES (BNFMRA), UK, AND AT THE LAQUE CENTRE FOR CORROSION TECHNOLOGY (LCCT), NORTH CAROLINA, USA.

* BNFMRA is now BNF-Fulmer.

Testing Conditions.

Velocity of Jet, 4.58 m/sec
Air added, 3 per cent by volume.
Duration, 28 days.
Water recirculated at BNFMRA
Not recirculated at LCCT.

Material	Average depth of attack (mm)	
	BNFMA	LCCT
Arsenical Admiralty Brass	0.34	0.27
Arsenical Copper	0.30	-
70-30 Copper-Nickel, 0.04%Fe	0.11	0.22
Aluminium Brass	0.04**	0.2
70-30 Copper-Nickel, 0.8%Fe	0.02	-
70-30 Copper-Nickel, 0.45%Fe	-	0.1
90-10 Copper-Nickel, 2% Fe	0.00	0.15

** One specimen out of 20 pitted to a depth of 0.65mm. No other specimen greater than 0.2mm.

greater attack in general than the recirculated water used in the UK trials.[9] Note, too, the beneficial effect of the high iron content in the 70-30 copper-nickel alloy.

General experience has shown that 90-10 copper-nickel can successfully be used in condensers and heat exchangers with water velocities up to 2.5 m/s. For pipeline systems, higher seawater velocities can safely be used in larger diameter pipes as indicated by codes of practice. BS MA 28, "Salt Water Piping Systems in Ships," for example, suggests a maximum velocity of 3.5 m/s in pipes of 100 mm diameter and larger, decreasing to 0.7 m/s in pipes of 10 mm diameter or smaller. For 70-30 copper-nickel, the maximum design velocity is given as 4 m/s for diameters of 100 mm or greater.

In practice, such guidelines have worked well because they take into account normal velocity raisers within pipe work systems, such as bends, etc., which can cause areas of higher flow rate.

Nevertheless, extreme turbulence has to be avoided. Instances where this may occur include tight radius bends, partial blockages and areas downstream of partially-throttled valves.

One theory, based on work carried out by Efird,[11] is that seawater moving over a surface creates a shear stress between the metal surface and the layer of seawater closest to it. As velocity increases, shear stress increases until the stress is such that it damages the protective film.

Efird studied and estimated the critical shear stress for various alloys. Shear stresses exerted vary with velocity and geometry as indicated by **Figure 7**. As pipe diameters increase, copper-based alloys tolerate higher nominal velocities.

Sato and Nagata[10] also showed that the shear stress at the inlet end of a condenser tube is double that found farther down, **Figure 8**. This indicates why copper-based alloys with higher resistance to impingement, such as the copper-nickels, are necessary to withstand corrosion problems in such areas.

Four-month tests by Kirk[12] using 102 mm ID, 90-10 copper-nickel, straight pipe work and long radius bends showed good resistance to a 7.3 m/s seawater flow velocity. This indicated that safe velocities may be higher than the 3.5 m/s maximum level often used in large-diameter pipe work, particularly when protective films are formed in clean, aerated seawater.

Although 90-10 copper-nickel pipe work may be limited to 3.5 m/s, the shear stress phenomenon helps explain why the alloy has been successfully used for ship hulls operating at 24 knots (12 m/s) with little thinning experienced. More work is necessary to explain the full extent of hydrodynamics on a flow system.

Other copper-nickel alloys have been developed and found to offer even better resistance to impingement attack. In particular, a 16.5%Ni-0.5%Cr alloy developed by INCO in the 1970s has a much higher, critical shear stress than the 70-30 alloy and is used for condenser and heat exchanger service. Also a 2% Mn-2% Fe, 70-30 copper-nickel alloy, developed for extra impingement resistance in situations where entrained sand is present in seawater, is now successfully used in the more demanding areas of desalination plants.

EFFECT OF SULPHIDES

Sulphides are present in polluted water either as industrial effluent or when water conditions support the growth of sulphate reducing bacteria. They can also occur in stagnant seawater by decomposition of organic matter to sulphides and ammonia.

Sulphides form a black corrosion product which is less adherent and protective than the normal oxide film. Under susceptible conditions, unwanted pitting or accelerated general corrosion may occur.

In the complete absence of oxygen, a sulphide film can show an acceptable degree of protection. Syrett found that corrosion rates still remain low in sulphide concentrations as high as 55 g/m^3 and velocities up to 5 m/s.[8] However, the sulphides become detrimental if dissolved oxygen is also present in the seawater, or if exposure to oxygen-free sulphide polluted waters is followed by exposure to aerated, unpolluted waters.

The presence of as little as 0.01 mg/l of sulphides has been shown to accelerate attack of 90-10 copper-nickel in aerated seawater, although the combined influence of velocity and sulphides makes the effect more significant. **Figures 9** and **10** illustrate this for 90-10 and 70-30 copper-nickels.(7)

Various explanations exist to describe how the corrosive influence of sulphides can be linked to the surface film. One explanation is that the sulphide film has been found by potential measurements to be galvanically more noble than the normal film. It is less adherent, and when damaged by impingement, the more active base metal is exposed and the corrosion rate is galvanically influenced.

Whatever the reasoning, the sulphide film which forms in polluted water will be replaced by a normal oxide film once the polluted seawater is replaced by clean, aerated seawater. This occurs when vessels are fitted out in polluted harbors and then operate in the open sea. Higher corrosion rates do continue for some time during the transition period. Syrett found that the transition can take nine days. Experience has shown that as soon as vessels begin regular operation, the normal protective film, once adequately formed, will also persist during subsequent harbor visits.

The ideal situation, whether in a ship or power plant, is to recirculate aerated, clean seawater at initial start up for sufficient time to form a good protective film. When formed, this provides a high degree of corrosion protection on subsequent exposure to sulphides.

In situations where it is not possible to use clean seawater, circulating the system initially with fresh water containing ferrous sulphate additive will encourage effective film formation.[13]

If polluted seawater is introduced at start up, it is important to keep the water circulating to enable aeration and to keep the pH at neutral or above. The system should be drained and air-blown dry for standby period of 3-4 days or more.

For situations where there is brief exposure to sulphides during normal operating service conditions, clean seawater should be returned as soon as possible. Normal harbor turnaround times, which often involve exposure to polluted water, have rarely led to significant corrosion problems.[7]

For other situations where the metal surface becomes exposed to sulphides under deposits or sediment caused by sulphate-reducing bacteria (e.g., where deposits are not removed from tubing), the remedy is simply properly scheduled cleaning. Such cleaning is usually scheduled at 2-6 month intervals and accomplished by water flushing or cleaning with nonmetallic brushes. This procedure is also necessary to restore optimum heat transfer.

Where there is long-term exposure to deaerated sulphide-containing seawater or regular (e.g., daily tide changes) alternating exposure to sulphide-polluted and aerated waters, copper-nickel is not generally recommended.

THE EFFECT OF SEAWATER TREATMENTS

Ferrous Sulphate

Ferrous ion additions are commonly used to reduce the corrosion of copper-nickel alloys either by a direct addition of ferrous sulphate or by means of a driven iron anode.

Ferrous ions in seawater are very unstable and can decay within as little as three minutes.[2] Therefore, the treatment is more effective when additions are continuous rather than intermediate.Ferrous ion treatment has been found to suppress the corrosion rates of copper-nickel in both polluted and unpolluted conditions. However, it is particularly attractive when sulphides are present in the seawater. For example, to encourage good initial film formation during fitting out, a system can be filled initially with fresh water containing 5 ppm ferrous sulphate and left in the system for one day. After this, the system can be used for normal fitting out purposes, but the ferrous sulphate solution (5 ppm concentration) should be recirculated for one hour per day throughout the fitting out period.[13] This practice is also useful when systems are retubed or renewed.

During normal service on ships, additional ferrous sulphate dosing is seldom required. Although if exposure to known polluted water is going to occur (e.g., when entering port), a reasonable additional precaution would be to add 5 ppm ferrous sulphate for one hour per day during the three days prior to entering, while in, and after leaving port. One treatment per week can be applied throughout a prolonged voyage.

Ferrous sulphate is not essential to successful performance but can be viewed as a remedy when trouble has occurred or as a precaution if trouble is likely. Most ships in service have operated successfully without any ferrous sulphate dosing.

Chlorination

Chlorine is used as an effective biocide when injected continually so that 0.2 to 0.5 ppm residual is maintained at the outlet tube sheet of a power plant condenser.[6]

Copper-nickel tubing is resistant to chlorination at concentrations normally required to control biofouling. Excessive chlorination, however, can damage copper alloy tubing.

There is some evidence that at high velocities, chlorination has the effect of increasing the impingement rate in the 90-10 alloy; although in 70-30, the rate is decreased.[7] **Figures 11 and 12** illustrate this effect, showing plots of chlorine level verses impingement attack in 90-10 and 70-30, respectively. An impingement jet velocity of 9 m/s was used. It should be noted, however, that 9 m/s velocity is not normally encountered or recommended for copper-nickel alloys.

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 and condensers. The fouling is usually most widespread in warm conditions and in low velocity (<1 m/s) seawater. Above 1 m/s, most fouling organisms have difficulty attaching themselves to surfaces unless already secured. There are various types of fouling organisms, particularly, plants (slime algae) sea mosses, sea anemones, barnacles and molluscs (oysters and mussels). In steel, polymers, and concrete marine construction, biofouling can be detrimental, resulting in unwanted excess drag on structures and marine craft in seawater or causing blockages in pipe systems. Expensive removal by mechanical means is often required. Alternatively, costly prevention methods are often employed, which include chlorination of pipe work 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 pipe work, water boxes, cladding of pilings and mesh cages in fish farming. A prime example of this was 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 or had suffered significant hull corrosion during that time.[14]

Efird, during the 14-year trials discussed earlier in the context of general corrosion rates in quiet, flowing and tidal conditions,(9) examined the final samples for biofouling. Both the 90-10 and 70-30 samples showed minimal fouling after removal from all three types of exposures, although different types of marine organisms appeared to adapt to different exposure conditions.

In quiet seawater, serpula, anomia, small barnacles and crisia bryozoa were found. For flowing seawater, barnacles, anomia and some serpia were observed, although they were of insignificant size. In the tidal zone, there were small serpulids and a few small barnacles, oysters and mussels.

During long-term exposure, therefore, some biofouling is possible. Another trial, again by Efird, examined more closely the progression of biofouling on immersed samples of 90-10 and 70-30 copper nickel over a five-year period.(15)

Plates, immersed from a floating dock at the LaQue Center for Corrosion Technology, showed very little fouling after 18 months, apart from slimes on both alloys. But after five years, fouling covered two thirds of the surfaces. The type of fouling was tunicates, bryozoa and serpulids. There was little to distinguish between the 90-10 and 70-30 alloys, **Figures 13** and **14**.

It was noted in the Efird trials that, at various intervals during exposures, the fouling would become detached and then new fouling would attach itself. It should be noted, however, that these trails were carried out under relatively sheltered conditions where slime layers are allowed to thicken to a point where biofouling can become attached. With the wave action on offshore platforms or with the normal flow velocities in cooling systems, the slime layer would not reach a thickness on copper-nickel to permit attachment.

Another study by Jackson at Langstone Harbour(16) in the UK looked only at 90-10 copper-nickel. This examined the exposure of four different test panels at two types of testing sites. The intention was to examine the biofouling behavior of cathodically-protected compared to freely corroding copper-nickel for structural sheathing.

The four panels are depicted in **Figure 15**. From left to right, the figure shows a steel panel attached to an aluminum anode, a cathodically-protected composite panel of steel with copper-nickel sheathing welded onto it, a copper-nickel panel protected by an aluminum anode, and a freely-corroding copper-nickel panel. A hole had been drilled in the composite panel with copper-nickel sheathing to expose a small area of steel.

One test rack was attached to a floating raft so that it would be immersed to the same depth of water, regardless of the tide. A second rack was attached to a sand bank and, therefore, was alternately immersed in seawater and then exposed to the atmosphere for 8-hour intervals every day. The raft trial lasted 137 weeks; the sand bank trial ceased after 378 weeks.

For the raft trial, it was found that slimes were formed on the steel before any of the copper-nickel surfaces. But, by the end of the first fouling season, biofouling was evident on all cathodically protected panels. This was in the form of sea squirts, sponges and, later, from weed. The fouling, however, could be dislodged more easily from the cathodically protected copper-nickel panel than from the steel.

The freely corroding panel developed a green, corrosion product film during the first weeks. There was minor attachment during successive fouling seasons, **Figure 16**, but these were lost during the following winter periods.

There was no preferential corrosion of the steel on the composite panel adjacent to where the copper-nickel was welded to the steel, and only superficial corrosion had occurred on the steel below the drilled hole.

This work shows how resistance to biofouling relies on the copper-nickel being in the freely corroding state. With cathodic protection, biofouling will occur, although organisms do not appear to attach themselves as tightly to copper-nickel as they would to steel.

On the half tide site, the pattern of fouling was different and took longer to develop. In the first few months calcareous deposits were formed on the cathodically protected copper-nickel. Barnacles were the first to colonize. On the composite panel this was initially on the welds, **Figure 17**, which had been made with a 70-30 consumable, indicating that the higher-nickel alloy (in the early stages at least) was less biofouling resistant. By 55 weeks, **Figure 18**, some fouling in terms of barnacles and weed was evident on all panels, although the freely corroding panel had significantly less. The barnacles on the protected copper-nickel were easily removed by a light rubbing with a finger.

After 378 weeks, all protected panels were well covered, and some biofouling was evident on the freely corroding panel, **Figure 19**. The fouling could be more easily removed from all the copper-nickel surfaces than from steel surfaces.

Like Efird, Jackson noted different types of biofouling after the different types of exposure. He also noticed signs of biofouling removal that went beyond the regular reduction found during the winter season, which was considered to be due to wave action.

Explanations for Biofouling Resistance

In the past, the need for copper and copper-nickel to be freely corroding to exhibit biofouling resistance has led researchers to believe that it is the copper ion entering the seawater that is toxic to marine organisms. Efird argued from his studies that this was incorrect because 90-10 and 70-30 copper-nickels corroded far more slowly than copper and still exhibited similar biofouling resistance over long-term exposures. He considered that it was the surface film, itself, which was inhospitable to biofouling.

The toxic-ion-being-released-into-sea-water theory was further disputed by Efird based on tests he carried out on

90-10 samples half-coated with nontoxic paint, **Figure 20**, over a period of 24 weeks. If leaching of copper ions was the phenomenon, some protection of the nontoxic surface would be offered. Due to the distinct cut-off line after 7 weeks, this did not appear to be the case. By 24 weeks, fouling on the nontoxic surface had started to creep above the copper-nickel which also, would not have been expected with the leaching theory.

Because it was found that, after extended time periods, the copper-nickel alloys tend to alternately lose and gain their fouling resistance, Efird concluded that the film is duplex in nature. It was thought that the initial cuprous oxide film is resistant, but when it oxidizes after extended exposure to form a green cupric hydroxychloride, fouling seems to increase. Because the second film is not so adherent, it can be easily removed, preventing secure attachment. Once sloughed off, the exposed surface is resistant again.

Microfouling

Copper alloys have good resistance to microfouling, although they are not totally immune to it. Microfouling can be found in heat exchanger and condenser tubing. **Figure 21**[8] shows the reduction in heat transfer for 90-10 copper-nickel that results from the growth of microfouling film on the inside wall in clean seawater at 1.8-2.4 m/s over 180 days. A 90- to 100-day interval between cleanings for copper alloys was indicated and it compared favorably with the 10-day interval found necessary for other alloy condenser tube in the study.

The ability of copper-nickel to resist microfouling and remain effective as a heat transfer surface in seawater for the 3- to 4-month normal intervals between mechanical cleanings, without chlorination, is of clear benefit and one of the reasons why copper-nickel continues as a useful tubing material wherever saline waters are used for cooling.

CONCLUSIONS

Both the biofouling- and corrosion-resistance properties of 90-10 and 70-30 copper-nickels appear strongly linked to the nature of the protective film formation on the alloys' surfaces. From various observations and studies, this film is complex and variable, although its importance is never in dispute.

The passive surface is responsible for high resistance to general corrosion, pitting, crevice attack and stress corrosion cracking. Resistance to velocity effects encountered under normal system flow rates is also good, although excessive turbulence may damage the protective film.

The inhospitable nature of the surface film is additionally thought to be the reason for biofouling resistance in copper-nickel alloys. To maintain this property, a freely corroding state is necessary.

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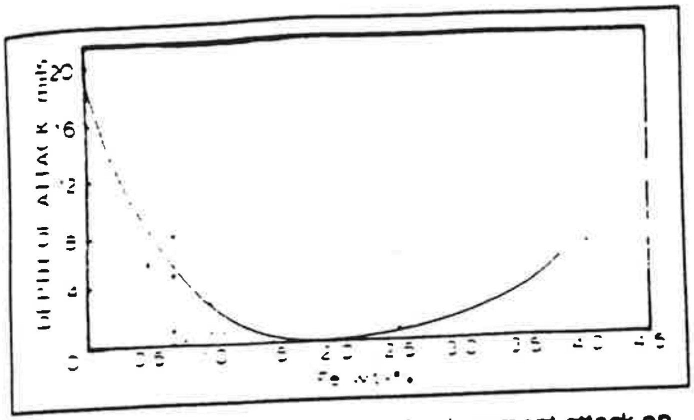

Figure 1 Effect of iron content on impingement attack on 90-10 copper-nickel in seawater; all data from 30 day tests, curve is best fit for data obtained at 3 m/s.(2)

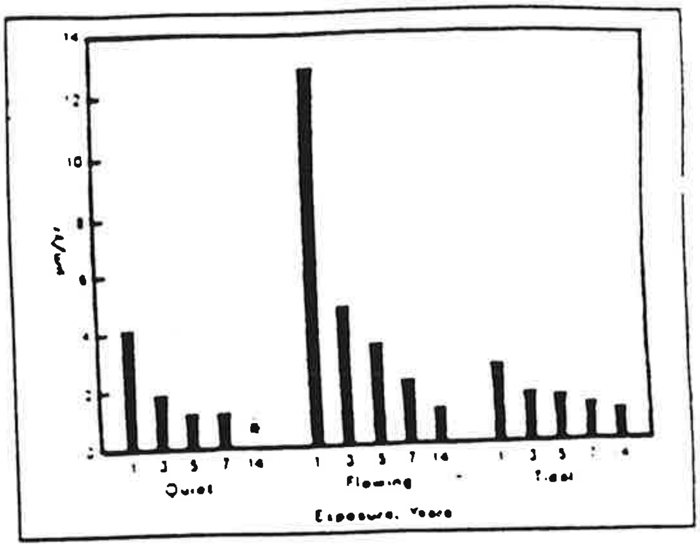

Figure 3 The change in corrosion rate with time for 90-10 copper-nickel in quiet, flowing and tidal zone seawater.

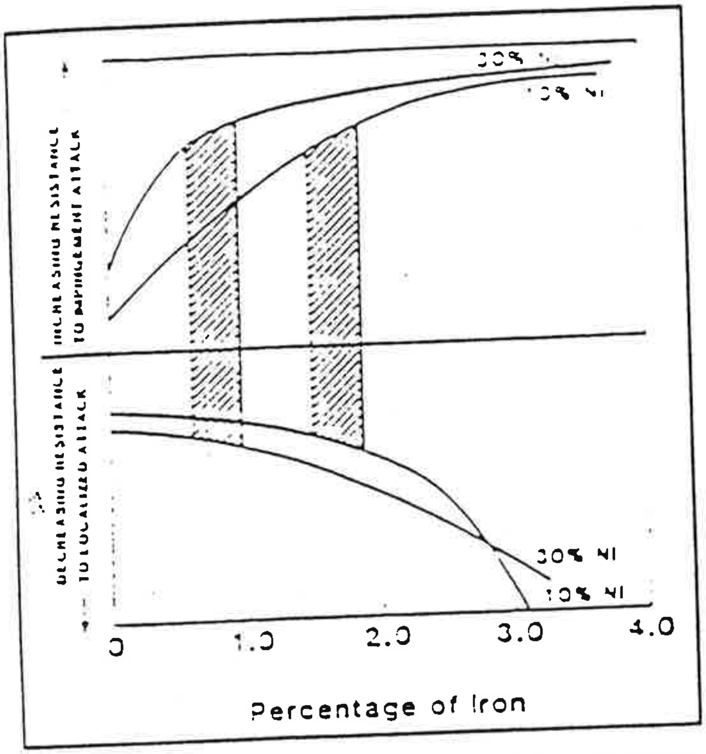

Figure 2 Corrosion resistance of copper-nickel alloys as a function of iron content.

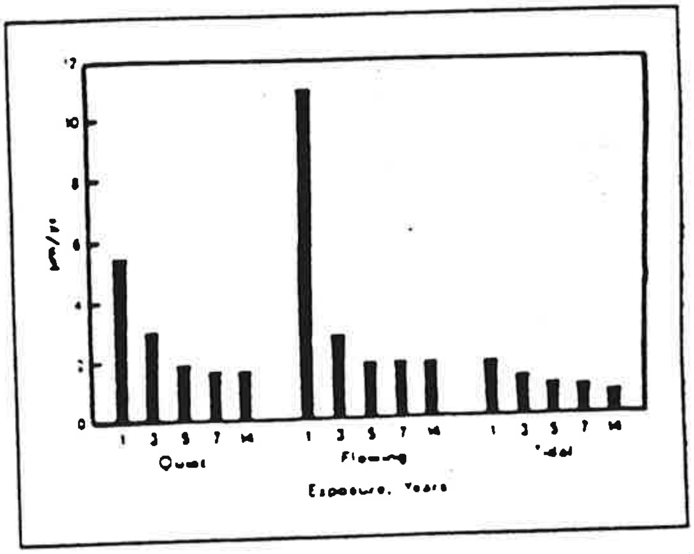

Figure 4 The change in corrosion rate with time for 70-30 copper-nickel in quiet, flowing and tidal zone seawater.

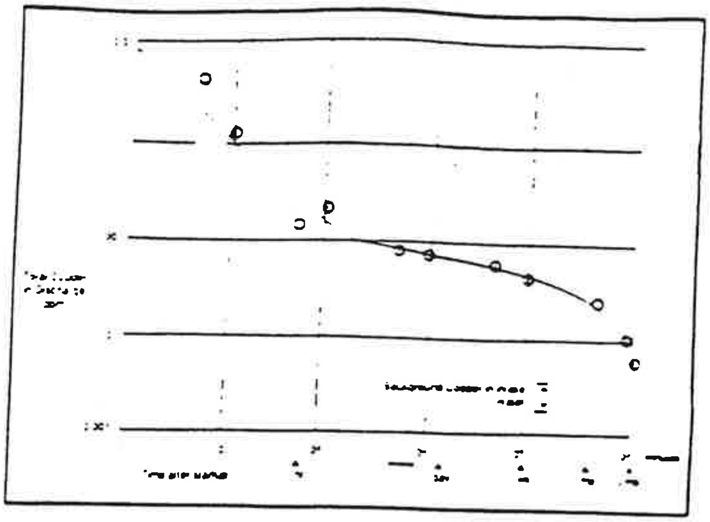

Figure 5 Formation rate of corrosion film on 90-10 copper-nickel in seawater.[6]

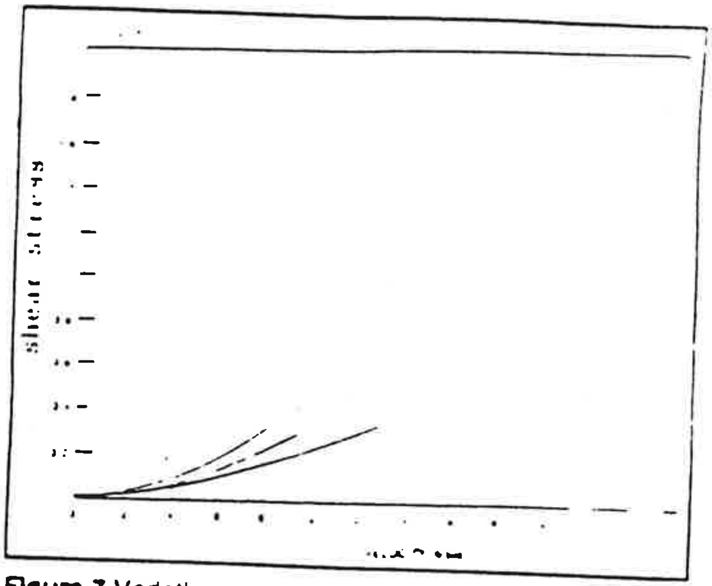

Figure 7 Variation in shear stress between in flowing seawater and metal wall with the nominal velocity in the pipe and diameter of the pipe.[11]

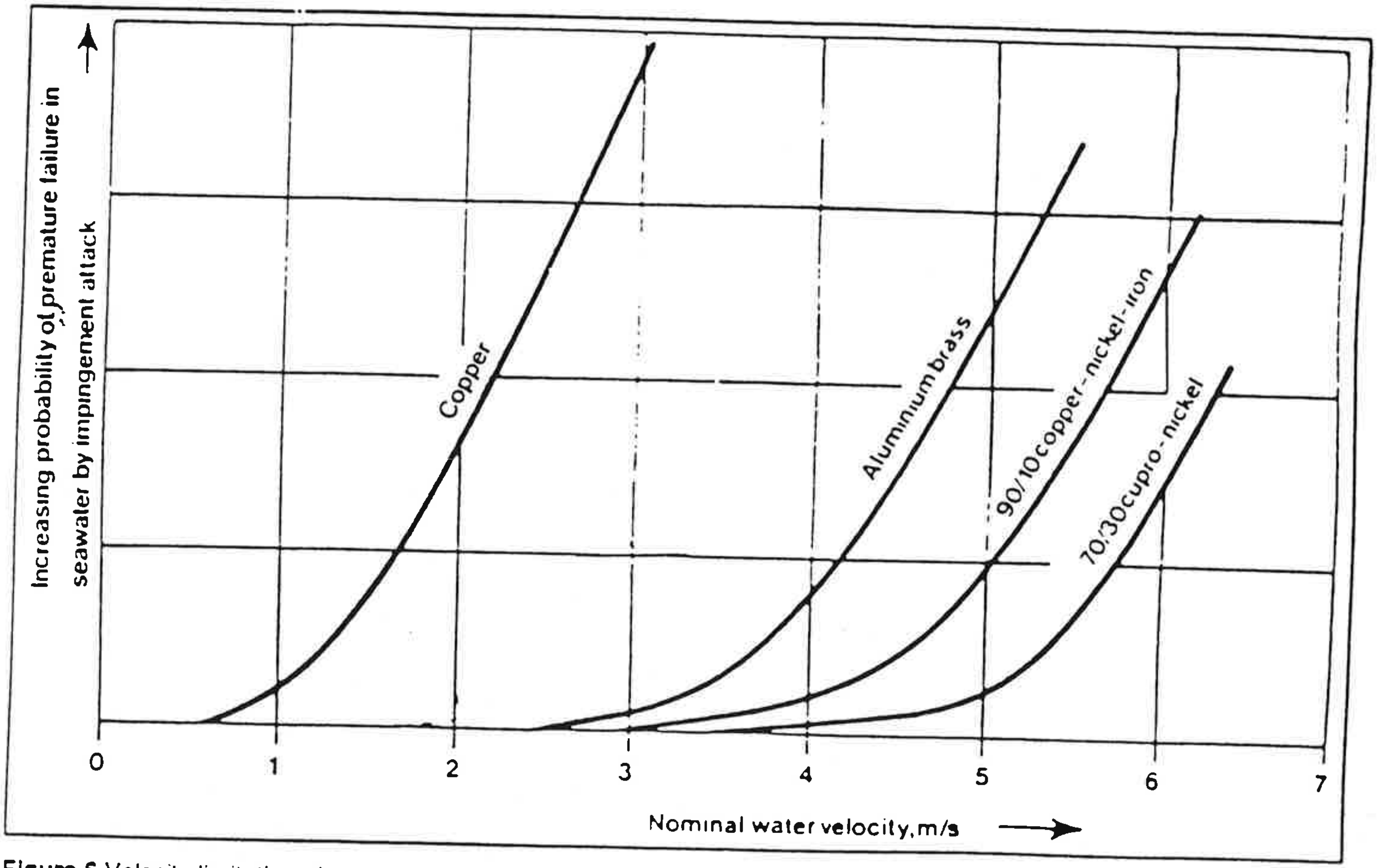

Figure 6 Velocity limitations for copper alloys in seawater.

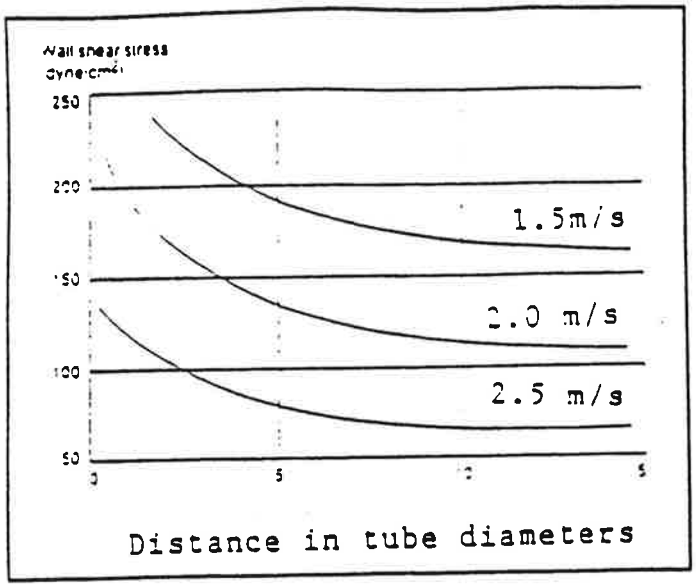

Figure 8 Variation of shear stress between the flowing seawater and metal wall with the distance from the inlet end.(10)

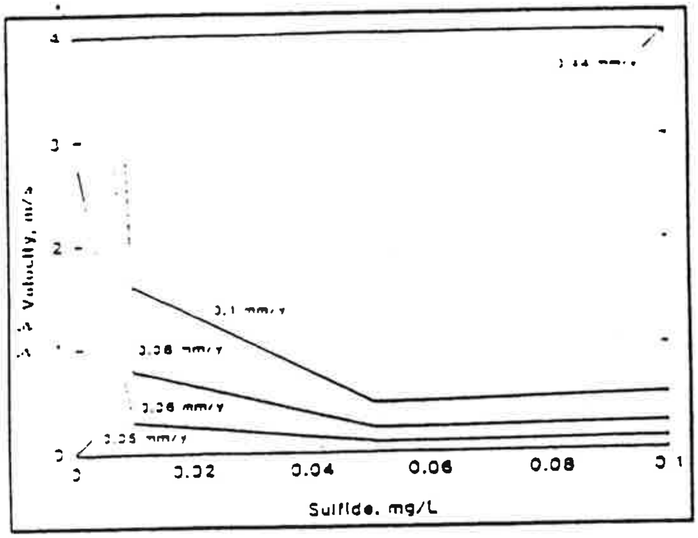

Figure 9 Corrosion rates for 90-10 copper nickel as a function of seawater velocity and sulphide content.

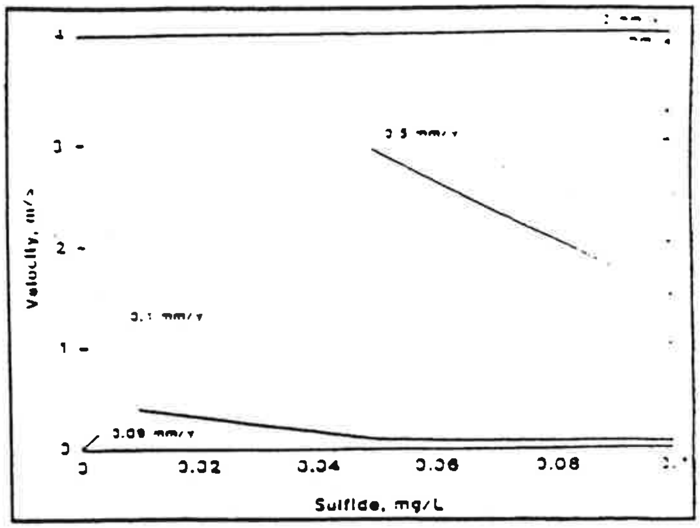

Figure 10 Corrosion rate for 70-30 copper-nickel as a function of seawater velocity and sulphide content.

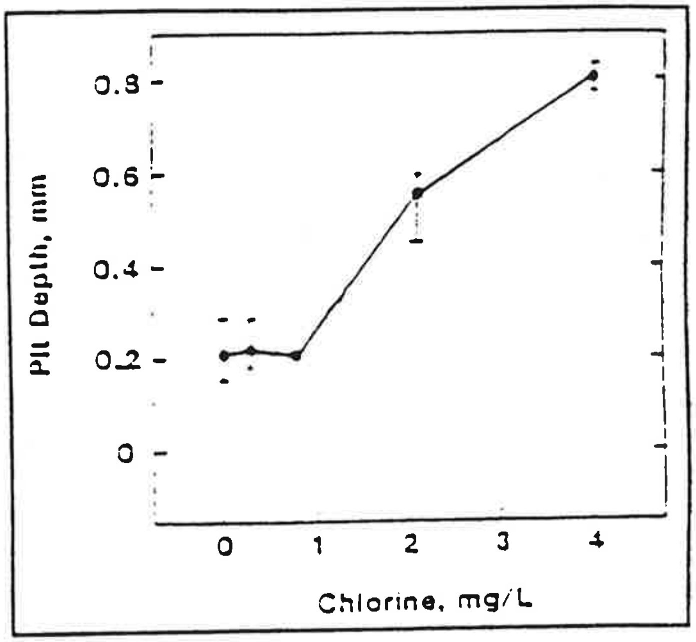

Figure 11 Depth of impingement attach versus chloride level for 90-10 copper nickel in seawater with an impingement jet velocity of 9 m/s.

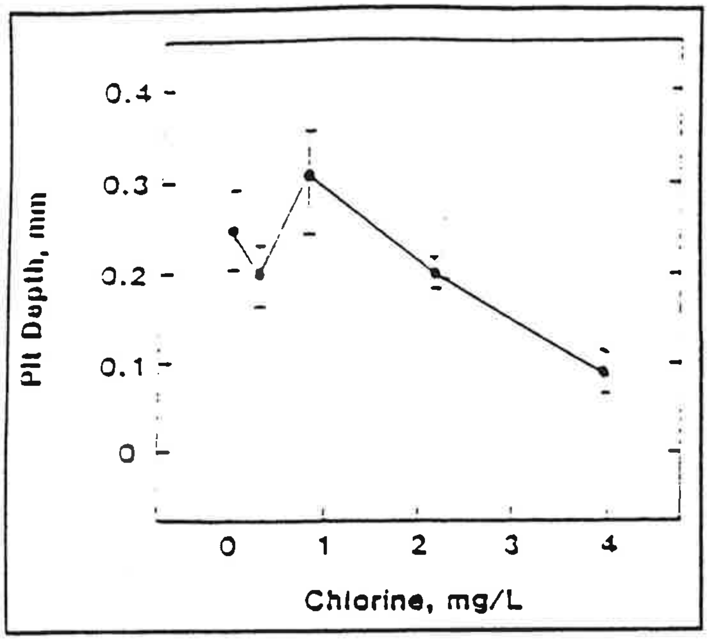

Figure 12 Depth of impingement attack versus chlorine level for 70-30 copper-nickel with an impingement jet velocity of 9 m/s.

Color plates, Figures 13 - 20, may be found on the following six pages.

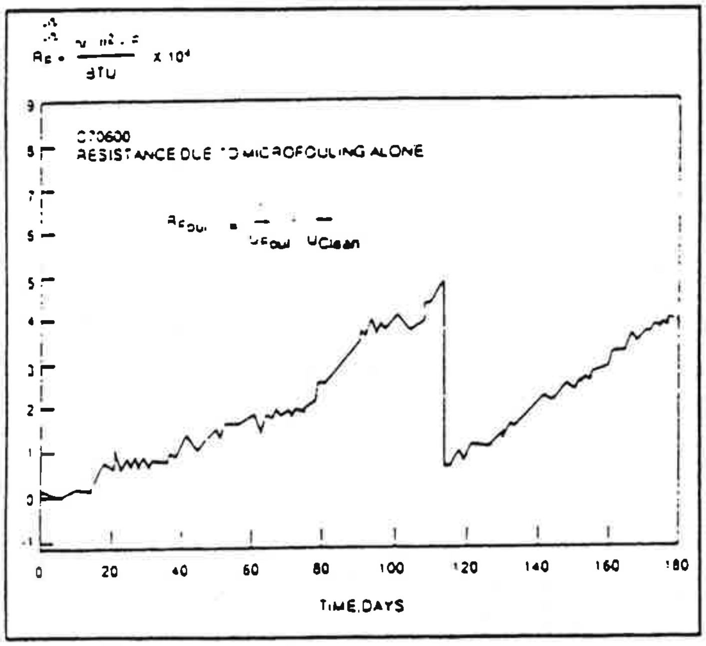

Figure 21 Resistance of 90-10 copper-nickel to heat transfer resulting from the growth of a microfouling film on the inside wall of tube in clean seawater.

Figure 13

The five-year sequence of fouling on 90-10 Cu-Ni (CA 706) in sea water.
Exposure periods are (from left to right):
Top—3 months, 9 months, 18 months.
Bottom—36 months, 48 months, 60 months.

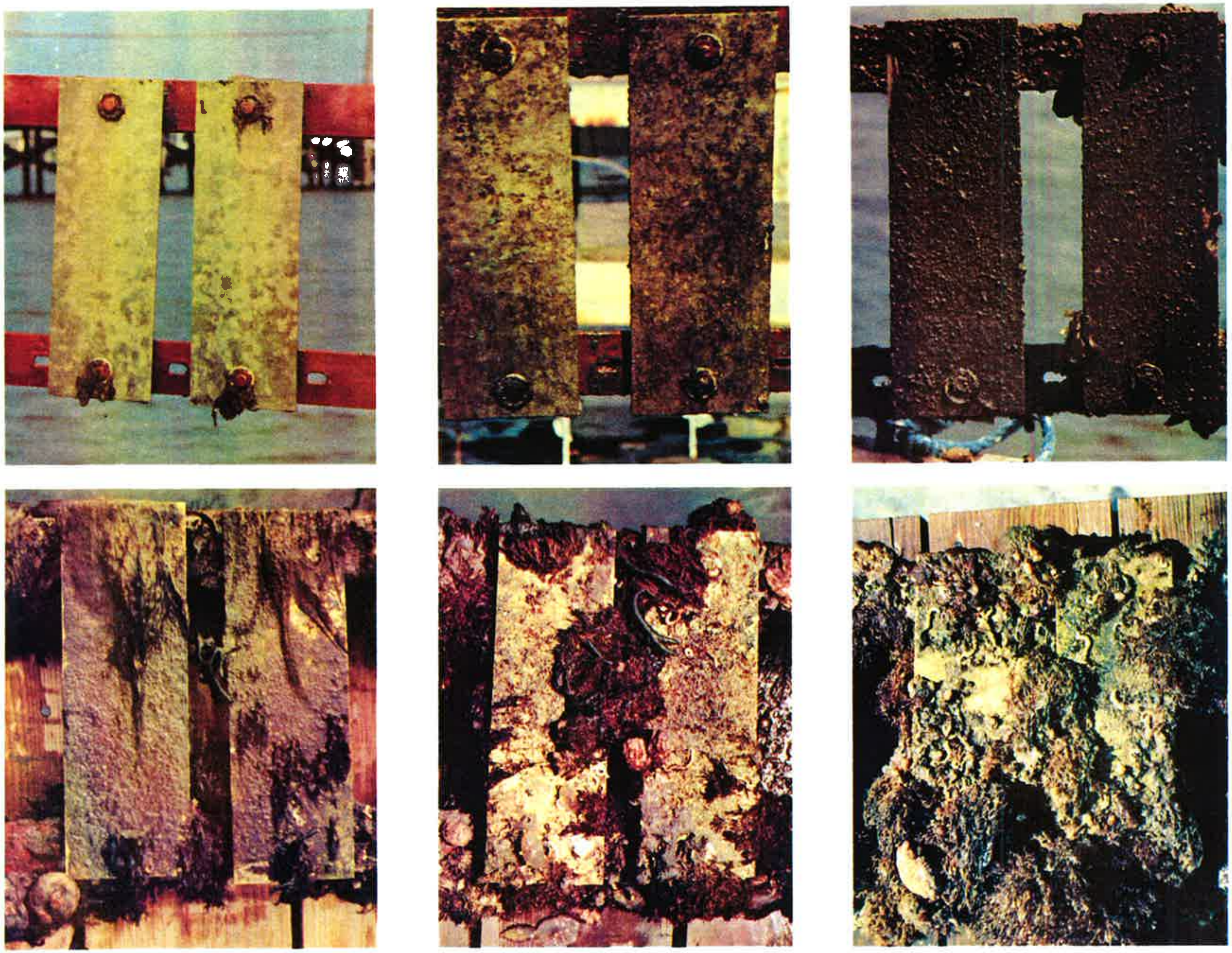

Figure 14

The five-year sequence of fouling on 70-30 Cu-Ni (CA 715) in sea water.
Exposure periods are (from left to right):
Top—3 months, 9 months, 18 months.
Bottom—36 months, 48 months, 60 months.

Figure 15.
Raft Site.
Mounted panels being
lowered into place.

Figure 16.
Raft site.
55 weeks immersion.

Figure 17.
90-10 copper nickel and 50D steel after 16 weeks on the half tide site.

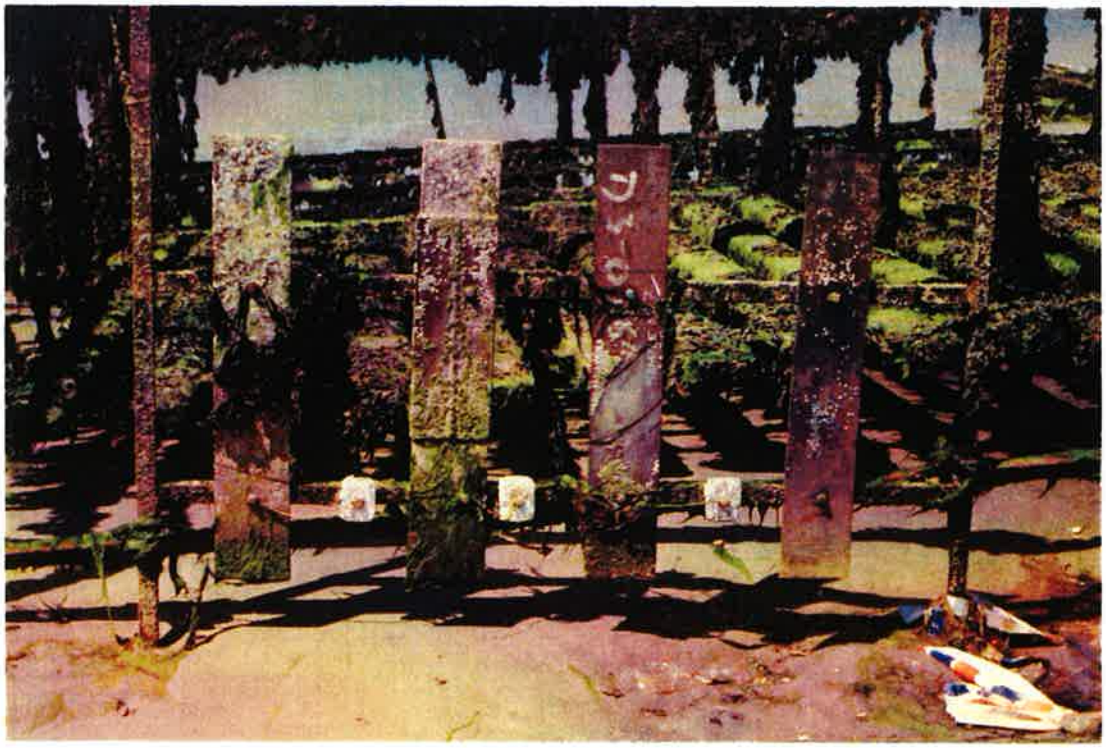

Figure 18.
55 weeks on half tide site.

Figure 19.

Insulated 90-10 Copper Nickel after 378 weeks on half tide site.

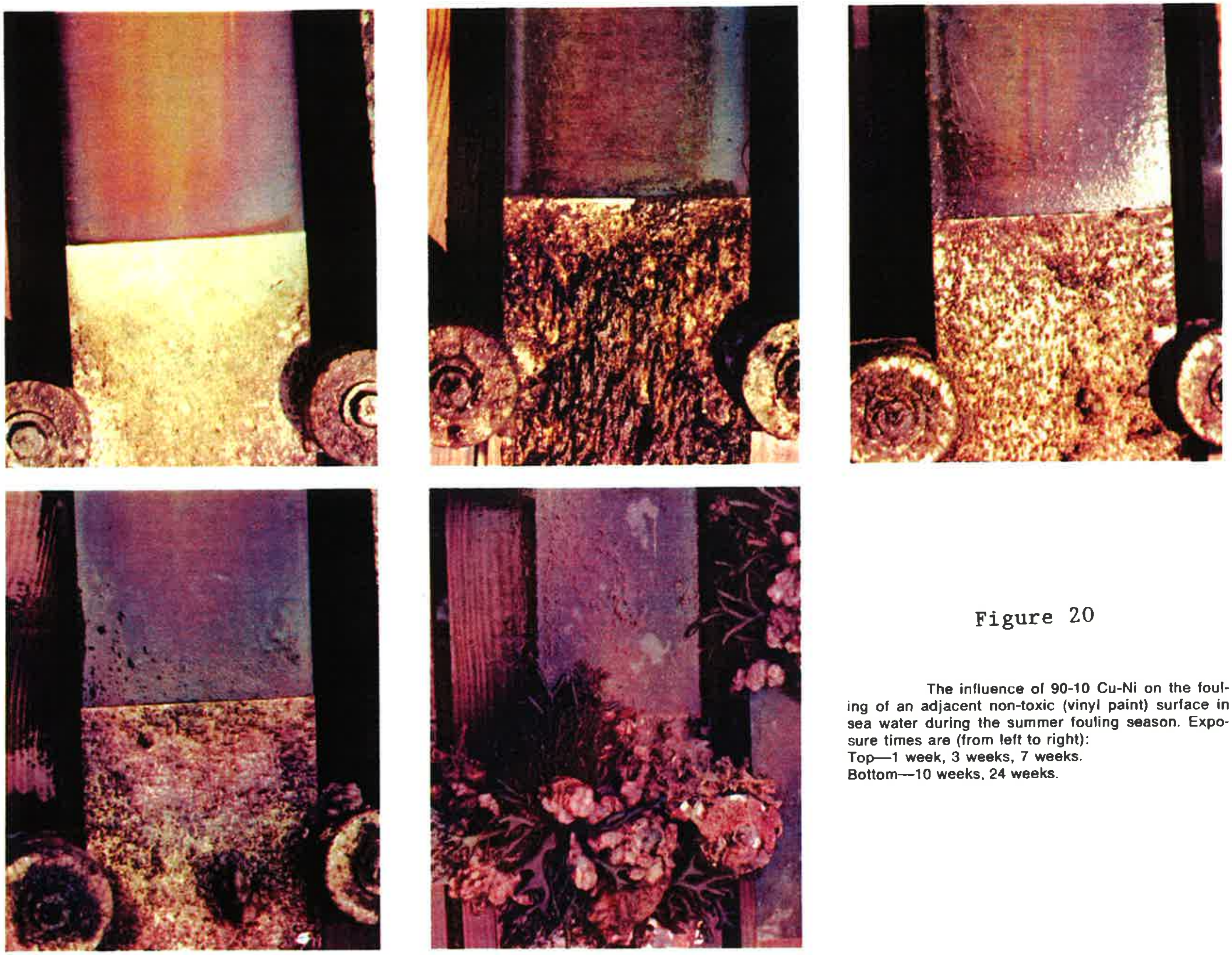

Figure 20

The influence of 90-10 Cu-Ni on the fouling of an adjacent non-toxic (vinyl paint) surface in sea water during the summer fouling season. Exposure times are (from left to right):
Top—1 week, 3 weeks, 7 weeks.
Bottom—10 weeks, 24 weeks.

MATERIALS SELECTION FOR HIGH RELIABILITY SEAWATER SYSTEMS

BRIAN TODD, Consultant to the Nickel Development Institute

Seawater systems are used by many industries such as shipping, offshore oil and gas production, power plants and coastal industrial plants. The main use of seawater is for cooling purposes but it is also used for fire fighting, oil field water injection and for desalination plants.

The corrosion problems in these systems have been well studied over many years, but despite published information(1) on materials behavior in seawater, failures still occur.

Economic factors have to be considered in selecting materials for these systems and in this context, essentially two types of system can be considered, as follows:

1. A low initial cost system largely based on carbon steel and cast iron which will require considerable maintenance over the life of the plant. Such a system is a reasonable choice in areas where labor costs are low and material is readily available.
2. A system based mainly on alloy materials which, if correctly designed and fabricated, will require minimum maintenance and will function reliably. Rising labor costs in most industries, together with the need for high reliability in capital intensive plant has produced a trend to this type of system.

In practice many systems are a mixture of these two logical approaches resulting in the high initial costs of one and the high maintenance costs of the other. For example, a plant which has experienced costly replacement to galvanized steel piping may replace it with copper alloy piping leaving valves fittings, etc., in carbon steel and cast iron. The resulting galvanic corrosion effects result in reduced life for these parts. Thus, higher initial costs have resulted in reduced reliability and high maintenance costs.

It is essential therefore in selecting materials for seawater systems to treat the system as a whole. This should include the heat exchangers where these are part of the system. However, this paper is confined to the seawater systems.

Another source of problems is the different requirements of plant builders and plant operators. The former, often bidding under competitive economic pressures, has to meet the normal one-year guarantee at minimum cost. Seawater, although corrosive, does not normally cause rapid catastrophic failures. For example, carbon steel immersed in seawater corrodes at about 0.1 mm/yr; whereas in, say, dilute acid, it corrodes at 100 times that rate. It is possible, therefore, to build a seawater system largely from carbon steel and cast iron to meet the guarantee requirement.

The plant operator, however, may require a 20-year trouble-free life but is often unwilling to specify the required material and accept the higher initial costs. It is not unusual to find a process plan successfully handling corrosive acids but shut-down because of problems in its seawater system which has not been given the same care in materials selection as the process equipment.

Materials selection for the two basic systems specified above are given in the following sections. It should be noted, however, that various studies of materials in seawater systems have concluded,(2-5) that systems based on alloy materials are more economic on a life cycle cost basis.

CORROSION CONSIDERATIONS

General

The corrosion behavior of materials commonly used in seawater systems has been reviewed by the author in **Reference 6**. Data from this review will be used in this paper and only two factors influencing corrosion behavior, namely velocity and temperature, will be considered here.

Effect of Velocity

Velocity is the most important single factor influencing design and corrosion in seawater systems. Velocity of seawater through the system influences pressure losses and thus pumping costs.

The design velocity chosen controls the dimensions of many components, for example, piping and valves. As the costs of these components increase rapidly with pipe diameter, then pumping costs and component costs have to be optimized. However, velocity also influences the corrosion behavior of the materials, and the design value chosen is often controlled by corrosion considerations. This is the case for carbon steel and copper-base alloys. However, for stainless steel systems, corrosion under flow conditions is not a problem.

Corrosion of carbon steel in seawater is controlled by the availability of oxygen to the metal surface. Thus, under static conditions, carbon steel corrodes at between 0.1 and 0.2 mm/yr, reflecting the oxygen level and temperature variations in different locations. Pitting also occurs.

As velocity causes a mass flow of oxygen to the surface, corrosion is very dependent on flow rate and can increase by a factor of 100 in moving from static (zero velocity) to high velocity (40 m/s) conditions.

Galvanizing confers only limited benefit under flow conditions, as corrosion of zinc also increases with velocity. For the thicknesses normally used in seawater piping, it will extend the life of the pipe for about six months.

The copper base alloys are velocity limited as impingement attack occurs when the hydrodynamic effect caused by seawater flow(6) across the surface of such alloys exceeds the value at which protective films are removed and erosion-corrosion occurs. Thus, these alloys, if they are to exhibit high corrosion resistance must be used at design velocities below this limiting value.

Stainless steels are not subject to impingement attack, but are prone to pitting and crevice corrosion under low velocity conditions and this must be taken into consideration when these alloys are used in seawater.

In recent years grades of stainless steel with high resistance to pitting and crevice corrosion have been developed. These are used for seawater system components such as piping and valves. These alloys are either: austenitic with about 20% chromium, 7% nickel and 6% molybdenum, plus nitrogen; or duplex with about 25% chromium, 7% nickel, 4% molybdenum and nitrogen.

Nickel base alloys such as Inconel™ Alloy 625, Hastelloys™ C-276 and C-22 and titanium are not subject to pitting or crevice corrosion in low velocity seawater, nor do they suffer impingement attack at high velocity. However, price limits their use to special applications in seawater systems.

Table 1 provides data on some of the materials commonly used in seawater systems. Details of composition are given in **Appendix 1**.

Because of the importance of velocity, it is usual in many systems to base design of pipe diameters on this factor and allowable design velocities are assigned to commonly used pipe materials.(7)

In considering velocity, it is important to note that local velocities may vary considerably from design velocity. This is particularly important where features of the system such as small radius bends, orifices, partly throttled valves, misaligned flanges, etc., which can generate turbulence, give rise to local high velocities which may accelerate corrosion. It follows that design and fabrication of the system should aim at minimizing turbulence raisers.

Effect of Temperature

Few data are available on the effect of temperature within the range normally encountered in seawater systems. It has been noted at the La Que Center for Technology that corrosion of carbon steel increases by approximately 50% between the winter (average temperature 7 C) and summer (27-29 C). Although oxygen solubility tends to fall with rise in temperature, the higher temperature tends to increase reaction rate. Evidence from work(8) on steel in potable waters suggests that the temperature effect is more important and corrosion, for steel, will increase with temperature.

For copper alloys, increase in temperature accelerates film formation; This takes about one day at 15 C, whereas, it may take a week or more at 2 C. It is important to continue initial circulation of clean seawater long enough for initial film formation for all copper alloys. More time is needed for winter than for summer start-ups.

For stainless steels and other alloys prone to pitting and crevice corrosion, increase of temperature tends to facilitate initiation of these types of attack. However, data on propagation rate(9) suggest that this declines with rise in temperature. The net effect of these conflicting tendencies is not always predictable. Temperature also influences biological activity which may, in turn, influence corrosion.

MATERIALS SELECTION IN SEAWATER SYSTEMS

PIPING

Low Initial Cost Systems

For low initial cost systems, materials such as mild steel, cast iron and steel with cement or organic coatings are used for piping. Data on steels show that the corrosion rate in flowing seawater increases from about 0.1 mm/yr under static conditions to almost 1 mm/yr at 3 m/s. As velocities in local areas of turbulence can easily exceed 3 m/s, even when the design velocity is much lower, corrosion tends to be accelerated in such areas. Also, as pipe thickness tends to increase with diameter, experience in systems with steel pipes show that failures commence first in the smaller diameters and, as the service life increases, failures occur on larger diameters so that repair costs accelerate with time. Cast iron behaves in a similar way to carbon steel. Small diameter steel or cast iron pipes are also easily clogged by corrosion products if not in continuous service.

Cement lined pipes are sometimes used. The main considerations here are:

1. Need for care in handling and fitting. If pieces of the

TABLE 1

EFFECT OF VELOCITY ON THE CORROSION OF METALS IN SEAWATER

Alloy	Quiet seawater 0-0.6 m/s		8.2 m/s Corrosion Rate mm/year	35-42 m/s Corrosion Rate mm/year
	Average corrosion rate in mm/year	Maximum pitting mm		
Carbon steel	0.075[•]	2.0	-	4.5
Grey cast iron	0.55 (graphitised)	4.9	4.4	13.2
Admiralty Gunmetal	0.027[+]	0.25	0.9	1.07
85/5/5/5 Cu Zn Pb Zn	0.017[+]	0.32	1.8	1.32
Ni Resist Cast Iron Type 1B	0.02[++]	Nil	0.2	0.97
Ni Al Bronze (BS 1400 AB2-C)	0.055[+++]	1.12	0.22	0.97
70/30 Cu Ni + Iron	< 0.02[•]	0.25	0.12	1.47
Type 316 Stainless Steel	0.02[•]	1.8	< 0.02	< 0.01
6% Mo Stainless Steel (typical)	0.01	Nil[++++]	< 0.02	< 0.01
Ni-Cu Alloy 400	0.02[•]	1.3	< 0.01	0.01

[•] 3-yr test at Harbor Island, North Carolina

[+] 42-month test at Freeport, Texas

[++] 6-year test at Kure Beach, North Carolina

[+++] 442-day test at Kure Beach, N.C. Alloy 10.6% aluminium, 2.5% iron, 5% nickel, 0.75% manganese.

[++++] 1-year crevice corrosion data on Avesta 254 SMO, Swedish West Coast.

All the above data (except velocity data for 6% Mo stainless steel) are taken from actual test results and are thus not exactly reproducible. This is particularly true of the maximum depth of pitting which may vary widely from test to test.

lining break off, the area of bare steel exposed is anodic to the steel embedded in the cement. Potential differences up to 400 mV have been measured(10) between embedded and exposed steel. The corrosion rate in such a cell will be determined by the flow of oxygen through the cement and, as the area relationship of embedded to exposed steel is high, the corrosion rate can be high.

2. Joints at valves and fittings. (Similar considerations apply as in item 1, above). All joints must be covered with a cement lining if corrosion is to be avoided.
3. Spalling off of linings. If corrosion occurs, then the corrosion product produced will tend to cause the lining to spall off and pieces of lining can partially block heat exchanger tubing causing local impingement attack. Physical damage can also cause the lining to spall with similar results.

Cement linings are most effective in long, straight runs of large (over 1 m) diameter. The ability to maintain lining integrity decreases rapidly with diameter, number of fittings and valves.

Other types of linings have been considered and sometimes used for seawater piping. A study by BSRA(11) on a wide range of pipe linings showed that only two, namely chlorprene and soft natural rubber withstood laboratory tests simulating shipboard conditions. In terms of piping costs they offered economic advantage over non-ferrous piping only in sizes above about 150 mm diameter. This study did not compare installed costs and Lim(12) found that installed cost of lined pipe on an offshore platform showed only a marginal cost advantage over 90-10 copper-nickel piping. The advantage in materials cost being offset by the extra care needed for installation.

High Reliability Systems

General

In marine engineering upgrading from steel has traditionally meant a change to copper-base alloys and this trend is also occurring for offshore oil and land based plants where high reliability is required. However, in recent years systems based on high performance stainless steels such as the 6% Mo superaustenitic and the super duplexes have been used by the offshore industry.

High reliability systems based on both copper-base alloys and stainless will now be considered.

Copper-Alloy Systems

Two copper-base alloys have been widely used for seawater handling, namely aluminum brass and 90-10 copper-nickel although in recent years, particularly for large diameter piping there has been a strong trend towards 90-10 copper-nickel. When using non-ferrous piping the system must be designed on the basis of water velocity in order to avoid impingement attack, even when some turbulence (which will give rise to high local velocities) may occur. **Figure 1**,(13) indicates how the probability of failure of impingement attack increases with design velocity. For a system with high reliability acceptable design velocities are as follows:

Copper	0.75 m/s
Aluminum brass	2.5 m/s
90-10 Copper-nickel	3.0 m/s
70-30 Copper-nickel	3.5 m/s

The use of 70-30 copper-nickel is confined to submarines where its high strength is advantageous. Due to the low design velocity and hence large pipe sizes, copper is uneconomical except for small diameter piping for essentially domestic applications, so that the real choice is between 90-10 copper-nickel and aluminum brass. Both materials are technically suitable, provided the system is designed to the water velocities given above and both have been successfully used in many seawater systems. However, the current trend is towards the use of 90-10 copper-nickel, the reasons for this being:

1. Its better weldability: Although aluminum brass can be welded using aluminum bronze filler materials, this is a relatively difficult procedure. Silver brazing is also used but this is expensive; firstly, because a high silver content (50% min) alloy is needed to provide the required corrosion resistance; and secondly, because the technique is difficult and time consuming for diameters above about 50 mm.
2. Its high stress corrosion resistance: 90-10 copper-nickel does not normally require any stress relief heat treatment after fabrication. Aluminum brass requires stress relief to avoid the possibility of stress corrosion cracking to which it is susceptible in seawater.
3. Its good experience: Gilbert(14) reports only nine cases of premature failure over a period of 20 years. This is a remarkable result considering the large tonnage of the alloy in use throughout the world. Only three of the failures involved excessive turbulence, suggesting current design velocities may be conservative.

It is also relevant to note that most of the world's naries have standardized on 90-10 copper-nickel for piping in surface vessels, thus ensuring worldwide availability of facilities for fabrication of the alloy.

Some use has been made of aluminum bronzes for piping in components such as pump columns. Nickel aluminum bronze is preferred for seawater, and usually in cast form (BS 1400 AB2C or UNS C95800). Care is needed with components fabricated from plate as the heat affected zones are sensitive to selective phase corrosion (dealuminification) which can lead to cracking. Risk of this can be reduced (but not eliminated) by heat treatment (at 650-675 C for six hours) after weld.

The design water velocities given above have been proved in service over many years and, as experience has been good, there has been a tendency to raise them to achieve economies in pipe costs. British Standard BSMA 18 allows up to 3.0 m/s for aluminum brass and 3.5 m/s for 90-10 copper-nickel pipe for bores above 100 mm. Below this size the velocity is reduced progressively. Although it is logical from a consideration of water flow through pipes, to expect a reduction in risk of impingement attack with increase in diameter and hence to allow higher water speeds in larger diameter pipes, there are few data on which to base design. One approach to this problem is to use the results obtained by Efird(15) which relate the onset of impingement attack to a critical shear stress (resulting from the flow velocity) and pipe diameter. If the value of critical shear stress of 43.1 N/m^2 (0.9 lb/ft^2) for 90-10 copper-nickel is accepted, then it is possible to relate critical shear stress to pipe diameter at a given seawater temperature.

Table 2 provides some data for seawater at 5 C (Higher temperatures would give higher critical velocities.)

The values in **Table 2** are based on parallel flow tests over plane specimens and, as would be expected, are higher than design water velocities which must allow for local turbulence effects. Thus, these absolute values should not be used as design values but could provide a guide to the designer to vary design water velocity with diameter to economize in system costs.

Stainless Steel Systems

Although all stainless steels have high resistance to flowing seawater, there is a need also for resistance to corrosion under static conditions and particularly in crevices such as flange surfaces and under deposits. Attempts to build seawater systems from standard grades of stainless steel such as Type 316, have proved unsuccessful. Pitting, particularly at or near welds and in crevices,(16) has often resulted in perforation within a few months. It is necessary, therefore, to chose an alloy with high resistance to localized attack which is often defined as an alloy with Pitting Resistance Equivalent Number PREN greater than 40. PREN is usually taken as Cr% + 3.3 Mo% + 16 N%.

TABLE 2
Effect of Pipe Diameter on Critical Velocity in Seawater at 5 C for 90-10 Copper-Nickel

Minimum Pipe Diameter (mm*)	Calculated Critical Velocity for Impingement (m/s)
72.15	4.70
103.00	4.85
154.25	5.08
212.30	5.25
315.00	5.42
447.20	5.52

* From Table 2 in British Standard BSMA 18.

The first successful major use of stainless steel for seawater systems was in the Gullfaks oil field in the Norwegian offshore sector where Avesta™ 254SMO (21% Cr, 18% Ni, 6% Mo, 0.2% N_2) was adopted. The reason for this selection was the need for a material resistant to alternate exposure to seawater and sulphide-containing oil in the storage/ballast spaces in concrete platforms.

Use of copper-base alloys, which lose corrosion resistance when exposed to sulphides, could not be considered.

TABLE 3

	Stainless Steel			Cupronickel		
	Size	Wall thickness mm	Weight tonnes	Size	Wall thickness mm	Weight tonnes
Seawater lift discharge from pumps: 6mm pipe * 3 flanges and 1 valve per pump	14"	4.78	2.7 (d)	20"	7.5	5.8 (d)
	14"	4.78	5.5 (w)	20"	7.5	11.5 (w)
Seawater lift header 180m straight pipe	20"	6.35	18.7 (d)	36"	8	37.7 (d)
	20"	6.35	77.9 (w)	35"	8	151.7 (w)

* (d) = dry
(w) = wet

As stainless steels are not sensitive to flow effects, a high design flow rate was chosen, 7 m/s. This limit was set by pumping costs and noise (cavitation). The resulting reduction in diameter of the piping reduced costs and also total (pipe and seawater) weight which is particularly attractive on offshore structures.[17] The effect of this can be seen from the data in **Table 3**.

Several thousand tonnes of superaustenitic stainless steel are now in service, mainly on offshore platforms.

A more recent development has been the use of superduplex stainless steel for a U.K. project – Ivanhoe and Rob Roy fields. The alloy selected was Zeron™ 100 (24% Cr, 7% Ni, 4% Mo, 0.2% N., 0.8% W). This has a PREN of over 40 and has high resistance to pitting and crevice corrosion. These systems are now in operation.

As well as the two already mentioned, there are now several high performance austenitic and duplex alloys available. **Appendix 1** gives typical compositions for several of these alloys.

VALVES

General

Many corrosion problems in seawater systems occur in valves. Often such problems are due to the use of steel or cast iron valves with non-ferrous piping. Although the life of such valves in a steel or cast iron pipe system is short (i.e., two to three years) when fitted in an alloy system, it may be less than a year due to the galvanic effects from the piping.

The three main components of a valve are the body, valve seats and the shafts or stems; these will be considered separately. It should be noted, however, in a system with a nominal seawater velocity of a few meters-per-second flow through the valve, that the valve, depending on its design, may give rise to turbulence and much higher local velocities, particularly when the valves are used for throttling.

Valve Bodies – Non-Ferrous Systems

The basic low cost valve used in ferrous pipe systems has a cast iron body with 60-40 brass internals. Depending on design, corrosion rates of several millimeters per year can occur on the body. The body cathodically protects the internals (until a layer of graphitic corrosion product forms) and the valve will function for two to three years.

Coatings on valve bodies are often used but their success depends mainly on the valve design (see later). In all cases, the life of the coating depends on its integrity, as manufactured, after installation and in service. Any break in a coating can result in intense corrosion and perforation or the valve body.

Upgrading of valve body materials to give higher reliability requires the use of alloys with good corrosion resistance. Such materials are Ni-Resist austenitic cast irons and copper-base alloys such as nickel aluminum bronzes, Admiralty and leaded gunmetals and cast copper-nickels. All these alloys are characterized by good resistance to static seawater (necessary for shut-down conditions) and to flowing seawater. **Table 4** gives some data under static and flowing conditions.

In relation to **Table 4**, it is interesting to note that in some cases, the corrosion at about 35–42 m/s is similar to that at 8.25 m/s. This indicates that impingement attack is occurring at the lower velocity and, under these circumstances, increase in velocity produces little increase in corrosion. The aim should be to use the alloy at a velocity lower than that causing impingement. Unfortunately, this cannot always be calculated so that where impingement is a possibility, alloys with high resistance such as nickel aluminum bronze or cast copper-nickel (plus chromium) should be used.

Ni-Resist iron valves are often used in ferrous systems to improve the valve reliability. They are also used in non-ferrous systems but copper-alloy valves are more common in such systems. Nickel aluminum bronze has high strength and this makes it attractive, particularly for large valves. Also, it has high resistance to impingement attack and this may be of importance in globe valves used under throttling conditions.

Valve Bodies - Stainless Steel Systems

Because stainless steels have high resistance to flow, then no problems will arise due to erosion-corrosion when used for valve bodies. The limitation to flow from corrosion considerations is set by cavitation which often occurs in seawater systems when flow is disturbed. Stainless steels have high resistance to cavitation but design velocities should be chosen to avoid severe cavitation within and downstream from valves. The 7 m/s valve used in the offshore industry takes cavitation into account.

As pitting and crevice corrosion are important in valves, then alloys with similar resistance to that of the piping are required for valve bodies. Cast versions of several of the high alloy stainless steels in **Appendix 1** are available and can be used for valve bodies. They can also be fabricated from wrought forms of the alloys.

Valve Seats and Stems – Nonferrous Systems

Valve seats, particularly those in throttling service, experience high water velocities, and data from **Reference 6** show that materials with high resistance to fast flowing seawater are stainless steels, nickel-base alloys and Monel alloy 400. Experience shows that when manufacturers upgrade the body material they often use the same materials for seats and stem as in a cast iron valve, i.e., 60-40 brass. Under these conditions the life of the valve internals is extremely short because, having lost the cathodic protection of the ferrous body, they fail by dezincification in a few months. **Figure 2** shows dezincification of a 60-40 brass stem from a bronze valve. This is probably the most common cause of failure in nonferrous valves. Although this type of corrosion is well-known, the rate of attack is often surprisingly high. The sample in **Figure 2** failed in less

TABLE 4

EFFECT OF VELOCITY ON CORROSION OF SOME CAST COPPER BASE ALLOYS AND NI-RESIST TYPE 1b

ALLOY	Quiet Seawater 0.06m/sec		Intermediate velocity 3.25 metre/sec	High Velocity tests 35-42 m/sec	
	General Corrosion in mm/year	Maximum pitting in mm	Corrosion in mm/year (60 day test)	Corrosion rate mm/yr (30-day test)	Remarks on low velocity data
88/10/2 Cu Sn Zn Admiralty Gunmetal	0.025	0.025	0.4 - 1.0	0.75 - 1.1	42 months at Freeport, Texas
85/5/5/5 Cu/Sn/Zn/Pb	0.018	0.030	1.0	1.3	•
Ni Resist Iron Type 1b	0.020	Nil	0.35	1.0	6 years at FLLCL
10/5/5 Al/Ni/Fe remainder copper	0.055	1.2	0.42	0.7 - 1.0	442 days at FLLCL
70/30 Cu Ni + 1.6% Cr	0.0010	0.28	0.22*	0.5	181 days at FLLCL

* At 15.3 Metres/sec

than one year – the original diameter was 25 mm.

Although stainless steel (AISI Type 316) will give good life in a non-ferrous valve, it is liable to pit (particularly in crevices) when the system is not in use and on a life cycle cost basis, the nickel-copper alloys are a better choice. Another problem with stainless steels is the frequent use of steels of lower alloy content than Type 316 and these can pit very rapidly in seawater. Such materials are 12% Cr (AISI Type 410) and 18% Cr (AISI Type 430) stainless steels. Use of these alloys in seawater systems often results in early failure.

In ball and butterfly valves, one of the seats may be non-metallic, e.g., an elastomer.

Inconel™ alloy 625 which has high resistance to both static and flowing seawater has been used as a weld overlay to produce highly resistant surfaces in critical areas of valves and shafts and also on pump castings. This alloy has excellent weld deposition characteristics and can be used as a general purpose overlay for avoidance of, or repair to, areas of corrosion damage in carbon, low alloy and stainless steel components.

Valve Seats and Stems - Stainless Steel Systems

Valve seats can be machined areas on the valve body, disc, gate or ball, depending on the valve design. In some cases separate seats are used so that they can be readily replaced in case of damage, for example, by a foreign body lodging between the surfaces. In such cases the seat material can be different from the body or disc material. For example, the greater hardness of a high alloy duplex stainless steel seat may be of benefit in a high alloy austenitic alloy component.

As described above, nonmetallic seats can also be used. Stems in stainless steel valves are made of materials with similar corrosion resistance to the body. The higher strength of duplex stainless steel makes them attractive for stems.

Effect of Valve Design on Materials Selection

Valves are a relatively expensive part of a seawater system but the cost of a valve depends on the design used. **Figure 3** shows some commonly used valve designs and gives an indication of their weight and pressure loss. Apart from any manufacturing difficulties, it is evident that a globe valve will be much more expensive than a butterfly valve because of its much greater weight. It will usually be more satisfactory to select reliable materials for valves, such as a butterfly valve, rather than to use an expensive design of valve, for example, a globe valve and try to economize on materials. Where the use of a globe valve is desirable, for example, for its good flow control characteristics, then the extra cost of corrosion resistant materials appropriate to the design must be accepted.

Some designers attempt to avoid corrosion problems by lining the valve. This is also related to the valve design; for example, butterfly valves are a simple shape and the body can be provided with a thick rubber lining which can be clamped firmly between the flanges joining the valve to the pipes and is not dependent on perfect adhesion between the rubber and the body. A gate or globe valve, however, is of complex shape and a lining, to be successful, must adhere perfectly to the metal surface. Experience shows that such adhesion is difficult to achieve and linings in valves of this type often have a short life.

A rubber-lined butterfly valve has certain features which must be considered in order to avoid corrosion problems. For example, the shafts, on which the butterfly turns, penetrate the lining and it is necessary to provide a positive seal between the lining and the stem to prevent access of seawater to the cast iron body. Failure to do this has resulted in valves failing due to corrosion products building up behind the lining causing seizure of the butterfly and stem.

Another commonly used seawater system valve is the membrane valve. This consists of a flexible membrane – usually of rubber – which separates the valve internals form contact with seawater. When operated, the membrane is extended into the stream restricting or shutting off flow. The shape is again simple and rubber linings on the body are effective. Cavitation damage to the rubber membrane can occur with severe throttling.

It is interesting to note the complex flow path within a globe valve. Several sharp changes of direction occur inside the valve and this gives rise to severe turbulence which can cause impingement corrosion on the valve body. Materials of high impingement resistance, such as nickel aluminum bronze or cast 70-30 copper-nickel, are recommended when this type of valve is chosen.

For stainless steel systems, turbulence in a globe valve presents no problem and alloys similar to the pipe materials can be used.

Table 5 provides a summary of materials suitable for seawater valves in non-ferrous systems.

Galvanic Considerations in Valves

From **Figure 4**, it is evident that all the copper-base alloys have similar potential and can be used together without fear of serious galvanic effects. Where carbon steel or cast iron bodies have been fitted with brass trim, these will have received considerable galvanic protection from the large area of ferrous material and may give a useful life. Upgrading the body material to copper-base alloys will, by removing the cathodic protection effect, give rise to corrosion of the trim.

It is good practice to arrange for the trim material to be cathodic to the body, hence the use of alloys such as Monel alloys 400 and K-500 and stainless steels.

The use of copper-alloy valves is desirable in copper-alloy pipe systems so as to retain galvanic compatibility. The use of unprotected ferrous valves in nonferrous systems should be avoided.

Non-ferrous valves are sometimes used in steel piping systems and while this will lengthen the life of the valve, galvanic corrosion of the piping adjacent to the valve may occur. A better choice of valve material in steel systems would be Ni-Resist cast iron as this is galvanically more compatible with steel, **Figure 4**.

For stainless steel systems, galvanic compatibility is not a problem in the system itself, even though different alloys may be used for different components. Care is needed, however, if the system is used to supply copper alloy heat exchangers as there can be a pronounced galvanic effect between stainless steels and copper-base alloys. This can be taken care of by fitting anodes in the waterboxes; iron, zinc or aluminum anodes can be used. Because iron ions in the seawater are beneficial for copper-base alloys, the use of iron anodes is advised.

SEAWATER PUMPS

Centrifugal pumps are normally used in seawater systems and are often driven by constant speed electric motors. At the normal speed of rotation, the tip speed of the pump impeller can reach 20 m/s and at this velocity, most copper alloys corrode rapidly in seawater. Fortunately, however, only certain components of the pump are exposed to these high velocities, and apart from these com-

TABLE 5

MATERIALS FOR SEAWATER VALVES IN NON-FERROUS PIPE SYSTEMS

Type of Valve	Body Material	Ball, disc or seat material	Stem Material
Butterfly valves	Cunmetals	5% nickel aluminium	Monel alloys 400 or K-50
	5% nickel aluminium bronze	Cast 70/30 cupronickel	Stainless steel (Type 316)
	Rubber-lined cast iron (provided a seal is fitted at the stem)	Cast Monel alloy	5% nickel aluminium bronze
	Cast 70/30 cupronickel Ni-Resist cast iron	Stainless steel (Type 316)	
Globe, gate or ball valves	As above, except that rubber lined valves should be avoided.	As above	As above
Membrane valves	Rubber lined cast iron.	Rubber (membrane)	Not critical as there is no seawater content.

• May pit in quiet conditions.

ponents, copper-base alloys can usually be used successfully in copper alloy systems.

For stainless steel systems, the pumps should be of similar materials. The main problem for stainless steel pumps is the shut-down situation. During operation, the risk of pitting and crevice corrosion is reduced as the metal surfaces are either exposed to fast flowing seawater or are subject to slight relative movement, which appears to discourage crevice corrosion. However, if seawater is left standing in the pump during shut-down, then pitting and crevice corrosion can occur. This can be taken care of by either arranging to flush out the pump with fresh water or operating it every few days.

Pump Casings

In copper alloy pumps, there is normally sufficient clearance left between the impeller and the casing so that the water flowing from the impeller does not impinge directly on the casing but is absorbed into the slower moving stream of water flowing over the metal surface towards the pump delivery pipe. Provided direct impingement is avoided, then materials such as gunmetals, aluminum bronze and cast 70-30 copper-nickels perform satisfactorily. However, there have been cases of premature pump casing failures in recent years(18) showing that direct impingement can occur. This may be due to increase in pump speed or the tendency to uprate the output from standard pump designs. Where such failures have been experienced, the life of the casing has been very short, for example, about 18 months. To avoid failures of this type, either the design must be amended so as to reduce seawater velocity at the metal surface, or materials of higher resistance must be used. Experience shows that cast 70-30 copper-nickel and 5% nickel aluminum bronze have higher resistance than gun metal or tin bronzes. Recent research, however, has shown chromium-containing 70-30 copper-nickel to have higher resistance than other copper-case alloys to fast flowing seawater, as shown in **Table 4**.

Where pump parts are fabricated by welding from nickel aluminum bronze plate, there is a serious risk of selective phase corrosion (dealuminification) in the heat effected zone of the weld. This can crack if stressed, e.g., by water hammer effects.

Stainless steel pumps can be made from cast versions of Type 316L (CF3M) or duplex grades similar to those listed in the **Appendix**.

Pump Impellers

The pump impeller is in contact with fast flowing, highly turbulent seawater and, for circulating pumps which are in use for most of the time, they should be made from a material with high resistance to these conditions. **Table 5** provides corrosion data in high velocity seawater for several pump materials.

It is clear from **Table 6** that the use of cast iron or mild steel can only be contemplated in pumps operated occasionally. From data in **Table 4**, Monel alloys 400 and K-500 and stainless steel Type 316 have very high resistance to flowing seawater, and cast versions of these alloys are preferred for pump impellers.

These alloys do not suffer from impingement attack but may pit when the pump is stationary and full of seawater. It should be noted, however, that the pitting likely to be experienced is often less severe than the general impingement corrosion which may occur at the tip of a copper-base alloy impeller and hence stainless steel or cast Monel Alloy 400 are preferred for this application. Alloy 20, and some higher alloy duplex stainless steel with higher resistance to pitting than Type 316 stainless steel are sometimes used for impellers in seawater service.

For Ni-Resist Type D-2 pump casings, cast stainless steel impellers are preferred. The Ni-Resist being somewhat anodic to stainless steel, gives a beneficial galvanic effect which lessens the risk of pitting on the impeller when the pump is stationary.

TABLE 6

CORROSION DATA ON MATERIALS IN HIGH VELOCITY TESTS

Alloy	Corrosion Rate mm/yr	Seawater Velocity m/s
Grey Cast Iron	13	38
Carbon Steel	9.5	40
Monel Alloy 400	0.010	43
Monel Alloy K-500	0.010	43
Stainless Steel (AISI Type 316)	0.005	43

For stainless steel pumps, the impeller can be made from the same material as the casing.

WATERBOXES

The most common materials for waterboxes are cast iron or mild steel, and these are often rubber or plastic lined to extend their life. Unlined boxes, as used in older installations, corroded and helped protect the tubes and tube plates. However, the corrosion of the waterbox itself is a serious problem and there is a trend towards non-ferrous boxes, particularly for condensers. **Figure 5** shows a fabricated 90-10 copper-nickel waterbox for a ship condenser. The use of this type of construction is economic, as all the external stiffening is carbon steel and only the metal in contact with seawater is copper-nickel.

Waterboxes in nickel aluminum bronze are also used, particularly with titanium tubes because of galvanic considerations. These are usually cast – fabrications require cathodic protection to avoid selective corrosion on welds (see piping section).

For small waterboxes, Ni-Resist irons can be used as this provides cathodic protection to the tube plates and tube ends but has a higher corrosion resistance than carbon steel or ordinary cast iron and thus has a longer life.

For stainless steel systems, waterboxes can either be rubber-lined carbon steel or made from the same materials as the piping.

STRAINERS

The purpose of strainers is to filter out materials detrimental to the system, for example, to minimize fouling and plugging of heat exchanger tubes.

Primary filtration is usually by a fairly robust grid or trash rack to eliminate large pieces of debris such as bottles and pieces of timber. These are usually made of steel or cast iron protected by paint and/or cathodic protection.

There is an increasing use of stainless steel (Type 316) for trash racks. This avoids the need for painting but cathodic protection is necessary to avoid pitting.

Trash racks are usually followed by stationary or traveling screens in the intake system and by fine filters within the system itself. Details of materials for these screens is given in **Reference 19**.

One important aspect of filtration is the removal of air from the system. Air can markedly enhance the erosion-corrosion effect of seawater and thus stimulate impingement attack on copper-base alloys. Provision should be made for air release from the high parts of components where it may accumulate, for example, waterboxes.

INTERACTIONS WITHIN THE SYSTEM

Galvanic Effects

Wherever possible, components of similar galvanic potential should be used for construction of the system. Where this is not possible, the following guidelines should be used:

1. Make the "key" component of a more noble material. For example, use copper-base alloy trim in a cast iron valve body.
2. Ensure that the material of lower potential is present in a much larger area than the more noble material so that the accelerated corrosion of the anode is spread over a large area.
3. Paint the more noble material. This can be beneficial as it reduces the cathode area even when the paint film is incomplete. An imperfect paint film on the anode would intensify attack at breaks in the paint.

Replacement of cast iron or fabricated steel waterboxes by rubber-lined or non-ferrous components will remove the beneficial galvanic effects on tube inlet ends provided by the ferrous components. This may lead to tube inlet end erosion, and either an alloy with higher impingement resistance should be used, or steel anodes should be fitted in waterboxes.

Titanium tubes have a strong galvanic effect on most copper-base alloys and can stimulate corrosion on copper-nickel waterboxes and tubeplates. Care is needed to avoid galvanic corrosion when titanium tubes are used – also for copper-nickel nozzles in titanium plate-type exchangers. The galvanic effects can be controlled by cathodic protection but care is needed to ensure that overprotection does not cause hydriding of the titanium tubes.(21)

Chemical Additions

Chlorine is often added to seawater to prevent marine growth which would cause tube blockage resulting in loss of heat transfer or impingement attack. Care must be taken in adding chlorine as excess chlorination can produce corrosion effects on steel and copper-base alloys. Work by Anderson and Richards(21) shows that control of fouling can be achieved without detriment to materials if the chlorination is carefully controlled. This is best done by measuring the residual chlorine at the plant outlet and adjusting the chlorine dose to maintain this at a low level, e.g., 0.1-0.2 ppm.

Another substance commonly found in seawater systems is the ferrous ion. In older systems with ferrous components, corrosion of these components provided a continuous supply of ferrous ions which, experience has shown, had an effect on corrosion of copper-base alloys, notably aluminum brass tubes. In modern systems, where the supply of ferrous ions may be largely eliminated either by use of non-ferrous materials or by use of coating, failures of aluminum brass heat exchange tubes have been experienced.(18) This can be rectified either by deliberately injecting ferrous ions into the system or by fitting copper-nickel tubes which are less affected by ferrous ions in the water.

CONCLUSION

By treating seawater systems as a whole it is possible to build corrosion resistant, reliable systems with low maintenance costs.

Table 7 summarizes the information in this paper and suggests materials which can be used to achieve these objectives or, by accepting higher maintenance costs and lower reliability, to build a system with minimum initial costs. It should be emphasised that systems consisting of partial adherence to the two approaches suggested are likely to result in higher initial costs and lower reliability.

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TABLE 7

SEAWATER PIPING SYSTEMS

Minimum first cost/high maintenance cost system	Component	High Reliability/low maintenance Cost System	
		Copper-Base	Stainless Steel
Galvanised steel	Pipe	90/10 cupronickel	6% Mo austenitic high alloy duplex
Steel	Flanges	Cast or forged 90/10 cupronickel. Steel welded overlayed with cupronickel Gunmetal.	6% Mo austenitic high duplex.
Cast iron or fabricated steel.	Waterbox	90/10 cupronickel with external steel reinforcement. Fabricated steel lined with 90/10 cupronickel. Ni-Resist cast iron (for smaller sizes)	6% Mo austenitic high alloy duplex.
60/40 Brass/Naval Brass	Tubeplates	Nickel aluminium bronze. 90/10 cupronickel.	6% Mo austenitic high alloy duplex.
Aluminium brass	Tubes	70/30 cupronickel (particularly2% Fe • 2% Mn) 90/10 cupronickel.	6% Mo austenitic high alloy duplex or titanium.
Cast iron or Leaded Gunmetal	Pump casing	Cast cupronickel. Nickel aluminium bronze. Admiralty Gunmetal. Ni-Resist Type D2.	See text.
Gunmetal	Pump Impeller.	Monel Alloy 410. Alloy 20 (CN7M). Stainless steel (CF3 and CF8). Nickel aluminium bronze.	See text.
Naval Brass	Pump Shaft	Monel Alloy 400 or 500. Stainless steel Type 316. Nickel aluminium bronze.	316 Stainless steel. 6% Mo stainless steel high alloy duplex.
See Table 4	Valves	See Table 4	See text
Cast Iron	Strainer body	Ni-Resist iron Type D2. Nickel aluminium bronze. Cast cupronickel. Gunmetal.	6% Mo stainless steels High alloy Duplex.
Galvanised iron	Strainer	Monel Alloy 400	6% Mo stainless steel. High Alloy Duplex.
Muntz metal	Plate	Type 316stainless steel (cathodically protected)	6% Mo stainless steels. High alloy duplex.

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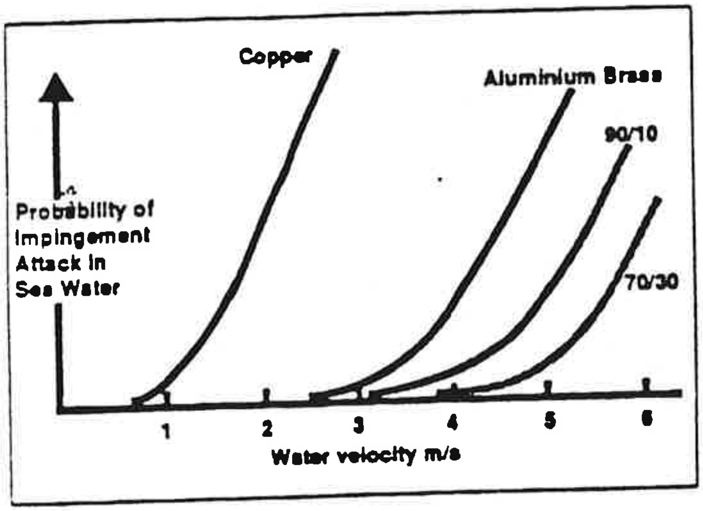
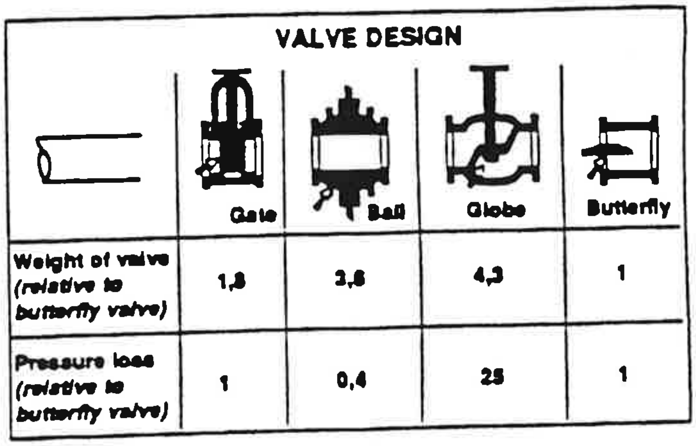


Figure 1



	Gate	Ball	Globe	Butterfly
Weight of valve *(relative to butterfly valve)*	1,8	3,6	4,3	1
Pressure loss *(relative to butterfly valve)*	1	0,4	25	1

Figure 3 Valve design

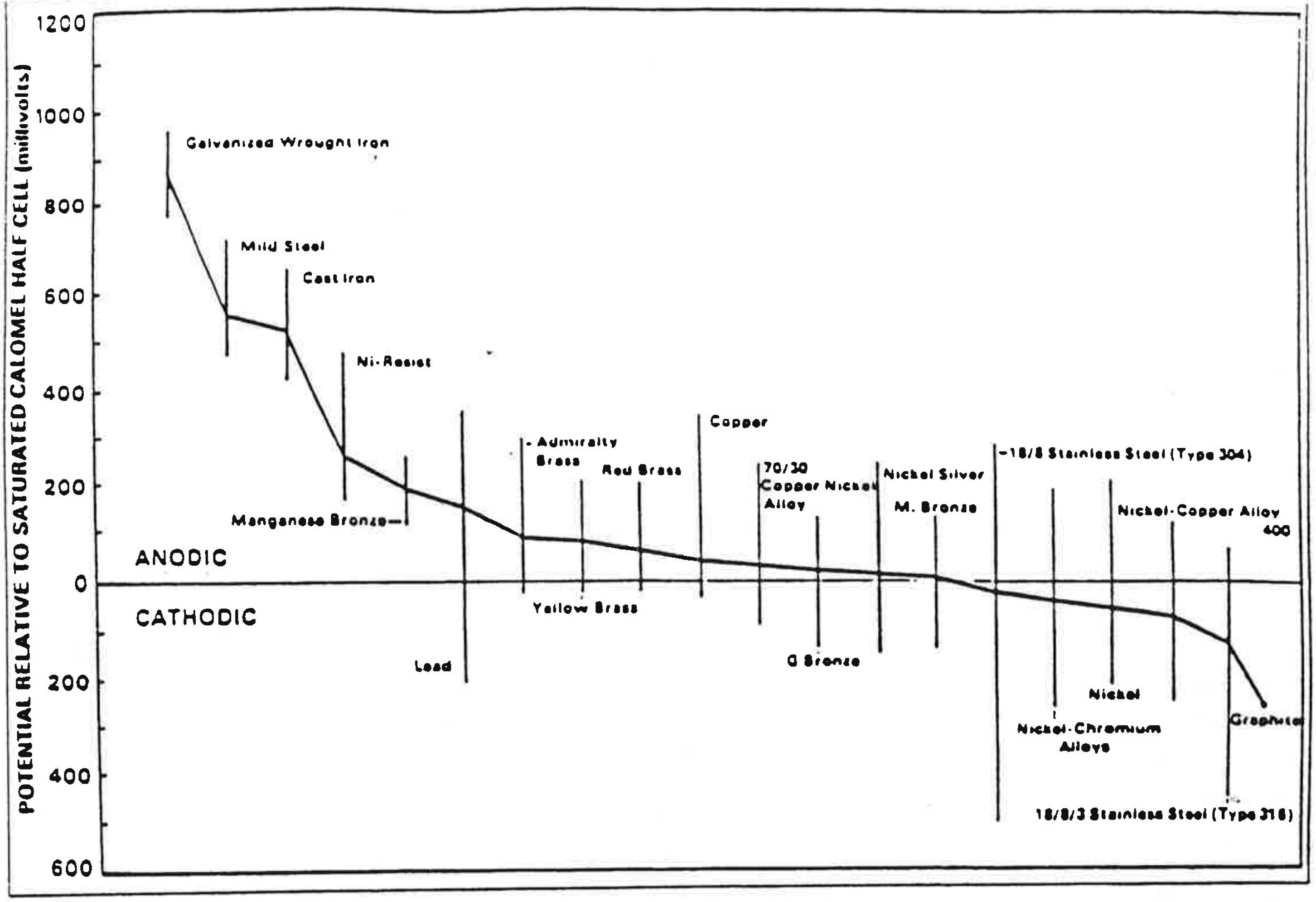


Figure 4 The galvanic series in seawater

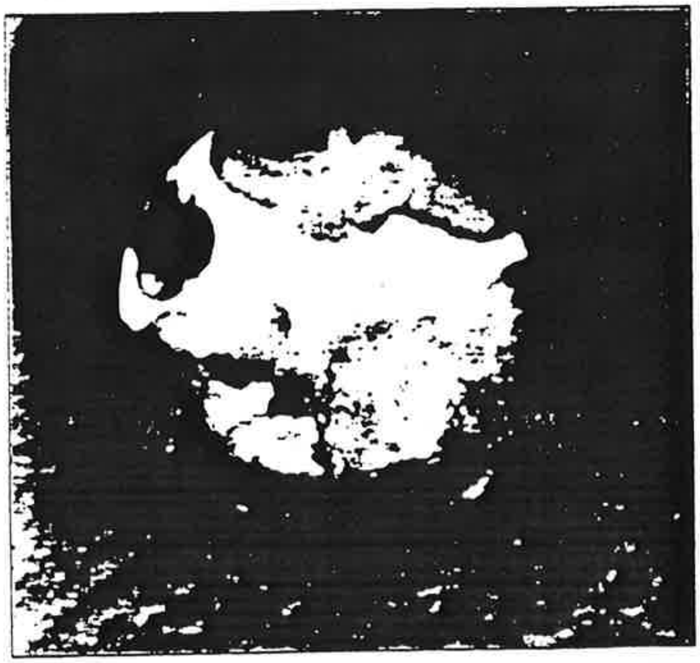


Figure 2 Dezineification of a Valve Stem made from 60-40 Brass

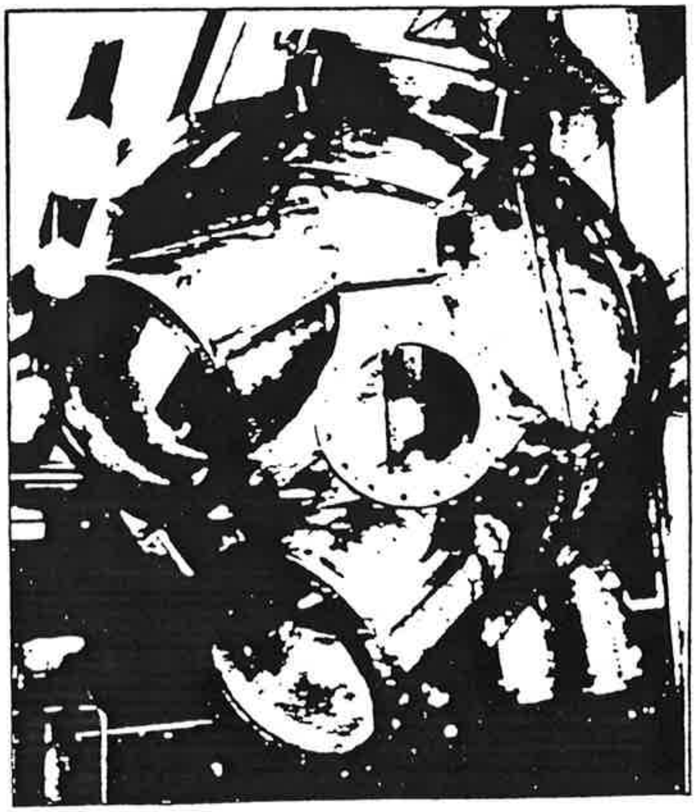


Figure 5 Fabricated 90-10 cupro-nickel waterbox

APPENDIX

TYPICAL COMPOSITIONS OF ALLOYS COMMONLY USED IN SEAWATER SYSTEMS

Standard Stainless steels and nickel-chromium-molybdenum alloys

Steel	Nominal composition per cent Carbon (max)	Chromium	Nickel	Molybdenum	Copper	Other
AISI Type 316	0.08	17	12	2.5		
AISI Type 316L	0.03	17	13	2.5		
ACI-CF 3M	0.03	19	11	2.5		
ACI-CF 8M	0.08	19	10	2.5		
ACI-CN 7 M (Alloy 20)	0.07	20	29	2	3	
Alloy 625	0.05	22	Rem	9		4 Niobium

Ni-Resist cast irons

Alloy	Composition per cent C max	Si	Mn	P max	Ni	Cu	Cr
Type 1	3.0	1.0 - 2.8	1.0 - 1.5		13.5 - 17.5	5.5 - 7.5	1.75 - 2.5
Type 1B	3.0	1.0 - 2.8	1.0 - 1.5		13.5 - 17.5	5.5 - 7.5	2.75 - 3.5
Type II	3.0	1.0 - 2.8	0.8 - 1.5		18.0 - 22.0	0.5 max	1.75 - 2.5
Type D-2	3.0	1.75 - 3.00	7 - 1.0	0.08	18.0 - 22.0		1.75 - 2.5
Type D-2B	3.0	1.75 - 3.0	0.7 - 1.0	0.08	18.0 - 22.0		2.75 - 4.0

Copper-tin, copper-aluminium and copper-zinc alloys

Alloy	Nominal composition per cent Copper	Tin	Zinc	Aluminium	Other
Admiralty Gunmetal	88	10	2		
Leaded Gunmetal	85	5	5	5	
Leaded Gunmetal + nickel	86	7	2.5		2.5% Lead 2% Nickel
Nickel aluminium bronze	85			10	5% Iron 5% Nickel
Aluminium brass	76		22	2	0.02% Arsenic

Alloys of nickel and copper

Alloy	Nominal composition per cent Copper	Nickel	Iron	Other
90/10 Cu-Ni	Remainder	10	1.5	1.0 Mn (max)
70/30 Cu-Ni	Remainder	30	0.6	1.0 Mn (max)
70/30 Cu-Ni (high iron)	Remainder	30	2.0	2.0 Mn
70/30 Cu-Ni + Cr	Remainder	30	0.7	1.6 Cr
Ni-Cu Alloy 400	31.5	66	1.35	0.9 Mn
Cast Ni-Cu Alloy BS 3071	30.5	66	1.35	1.6 Si
Ni-Cu Alloy K 500	31.5	66	1.35	0.9 Mn 2.8 Al 0.5 Ti
Cast Ni-Cu Alloy BS 3071 NA3	29	64	2.0	4.0 Si

High Alloy Austenitic and Duplex Stainless Steels

Alloy	Producer	Cr%	Ni%	Mo%	Cu%	N%	PRE_N
AL-6XN	Allegheny	21.0	25.0	6.5		0.20	45.6
Uranus SB 8	Creusot-Loire	25.0	25.0	5.0	1.5	0.15	43.9
254 SMO (UNS S31243)	Avesta	20.0	18.0	6.1	0.7	0.20	43.3
A 965 (UNS S31254)	VEW	20.0	18.0	6.1	0.7	0.20	43.3
HR 8N	Sumitomo	21.0	24.5	5.8	0.8	0.20	43.3
AL-6X (UNS NO8366)	Allegheny	20.0	24.5	6.3			40.8
Cronifer 1925 HMO (UNS NO8925)	VDM	21.0	25.0	5.9		0.14	42.7
Sanicro 28 (UNS NO8028)	Sandvik	27.0	31.0	3.5	1.0		38.9
Alloy No. 20 Mod (UNS NO8320)	Haynes	22.0	26.0	5.0			38.8
Zeron 100*	Weir	25.0	7.5	3.8	0.7	0.25	> 40
SAF 2507	Sandvik	25.0	7.0	4.0		0.25	> 40
Fermanel	Langley	27.0	8.5	3.0	1.0	0.25	> 40
Uranus 47N	Creusot-Loire	25.0	6	3.0	0.5	0.20	> 38

* Also contains 0.7% W

COPPER-NICKEL CONDENSER AND HEAT EXCHANGER SYSTEMS

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INTRODUCTION

For the vast majority of heat transfer equipment applications, the transfer of heat takes place between two fluid streams. The heat exchanger is simply a device which directs the flow paths in such a way that the two streams are brought into thermal contact through a conducting wall while being kept physically separate. This thermally conductive wall is the tube-in-shell and tube type heat exchangers that make up a large percentage of such units in power plants, ships, the chemical process industry and in desalination. The relatively thin-walled tube, selected primarily for heat transfer efficiency, becomes the critical component in condensers and other heat exchangers and must perform well over long periods of time under sometimes very difficult operating conditions. Copper-nickel alloys have established a long and successful history in seawater cooled heat exchangers and will be emphasized in this paper.(1-7)

Since the condenser is the heart of the heat reject system in operating power or process industry plants, as well as in ships, its reliability and efficiency affect the overall system performance. Deposits and films which accumulate and grow on the tube's inside surface affect heat transfer capacity and in turn its ability to condense steam. This paper will discuss the influence and control of these films as important parts of tube integrity that maintain the interface between a highly controlled thermodynamic working fluid and a potentially aggressive cooling water. Natural seawater, that may or may not be polluted, will be considered the cooling water for all discussions. Coastal plants are usually designed to have one large heat exchanger with seawater on the tube side and multiple, closed loop cooling systems on the shell side. Heat exchanger materials must be selected to handle steam or other working fluids in these shell side circuits, as well as the available on-site cooling water on the tube side. While these closed loop circuits have their own criticality in terms of thermodynamics, mechanics and operating maintenance, this paper will concentrate on the tube-side (seawater) characteristics. Any leakage from the tube side will readily contaminate whatever working fluid is on the shell side. The effects of contamination must be considered throughout the process, from design to materials selection to maintenance, for the operating age of the total system.

In regard to tubing performance, several interactions with other components of the cooling water system must be considered:

1. First in importance is the debris removal equipment ahead of the waterbox or channel head. This is discussed in more detail in the section on the Intake System.
2. The design and operation of the chlorine injection system is discussed in the section on Corrosion Resistance. Even after extensive screening out of debris and marine organisms, free swimming larvae enter the waterbox and tubing and can attack and grow if given the opportunity.
3. The design velocity and flow pattern from the waterbox through the tube bundle can affect the corrosion and heat exchange performance of the tubing. Refer again to the section on Corrosion Resistance.
4. Galvanic interactions among the materials of the waterbox, tube sheet and tubing are also discussed in the Corrosion Resistance section.

WATER QUALITY

Usual seawater analyses will include temperature, salinity or conductivity, dissolved oxygen, pH and sometimes metal ions if a known source is nearby. The presence or absence of oxygen, hydrogen sulfide (H_2S) and industrial pollutants (especially ammonia) are compositional factors that have a significant effect on copper alloy performance in heat exchanger systems and must be identified. While not normally included in water analyses, the debris loadings (sticks, stones, gravel, sea shells, mud and sand), dissolved gases and free swimming larvae of the biofoulers often have a far greater effect on tube performance than the compositional factors reported in the usual water analyses.(8-10) Water pollution increased in the United States around mid-century under the dual impact of industrial waste and untreated municipal sewage until the 1960s. Federal and state legislation then reversed this trend, and concurrently pollution related tubing failures that had peaked in the early 1960s began to decline.

Environmental legislation has had other effects on the handling of cooling water.(11) At the point of discharge, both temperature and the manner in which the discharge water is dispersed is usually regulated to a maximum temperature differential in relation to the ambient temperature of the receiving body of water. In addition, the Environmental Protection Agency (EPA) limits residual chlorine to 0.2 ppm average in effluent streams.

The net effect of the environmental legislation was a change in the corrosive nature of the cooling waters. It increased biofouling activity once again, so that the full impact of biofouling had to be dealt with in existing installations as well as the design of new ones.

INTAKE SYSTEM

Design, operation and maintenance of the seawater intake system has a profound effect on heat exchanger tubing performance. Shipboard systems are relatively simple, since ships operate in large bodies of water with very low debris loadings and quite clean seawater, except in port. These intake systems include a grate, flush with or slightly recessed in the hull, to keep out large items such as boxes, fish or floating logs. Stationary screens or strainers are normally provided between the pumps and the waterbox to screen out smaller debris. Additional screens with small openings are essential ahead of small diameter tubes in auxiliary exchangers such as oil coolers and keel coolers.

The design of the intake system for coastal plants is much more elaborate and more critical. **Figure 1** illustrates the function of bar grates and traveling screens. Large floating debris is kept out of the inlet by the bar grates. Water velocity through the bar grates must be low enough so that fish and trash are not held against the screens, thereby reducing the flow area and increasing velocity through the screens. Any increase in water velocity will simply hold more trash and fish, further reducing flow area and further increasing water velocity.

The traveling screens downstream of the bar grates are designed to screen out fish, crab claws, sea shells, twigs, polyethylene bags and similar trash. These screens are designed to discharge accumulated trash as they slowly rotate. Traveling screens must be maintained in good operating order. The hole size in the travelling screens is on the order of 12 mm or less, and the heat exchanger tube size is usually set at a minimum of two times the screen opening.

Figure 2 illustrates the section of the cooling water system between the traveling screens and the exchanger or condenser. The stationary screens, which may be basket or automatic strainers or filters, provide the final screening of debris before the cooling water enters the waterbox and tubing. **Figure 3** is a photograph of two such basket-type strainers in a Mideast desalination plant. The coarse debris, shells, rocks, glass, a nail and a piece of steel in the upper part of **Figure 4** were removed from the bottom of one of these two strainers. Shells and smaller stones shown in the lower part of **Figure 4** were removed from the discharge side of the tube bundle. The screen in the strainer had been broken by the larger rocks, nail and steel, allowing the latter mentioned debris to reach the tubes. Screen openings were 9 mm, which kept debris large enough to cause lodgements out of the tubing until the screens were broken. Some of the debris had lodged in the tubes leading to penetration of the tubing downstream of the lodgements, similar to that shown in **Figures 5** and **6**.

The desalination plant operators identified and recorded the failures as tube failures; whereas, they were really screen failures. It is absolutely essential that screens in the intake system be properly designed, and it is equally essential that they be properly operated and maintained. Tube failures from debris lodgements are *screen failures* and should be recognized as such. Otherwise, the real cause of failures may be overlooked and quite unnecessary tube failures allowed to continue.

With two strainers, as in the above mentioned design, the plant operates one until it is plugged and then switches to the other. The strainer removed from service must be thoroughly cleaned and the screens repaired or replaced so that the strainers, not the tube bundle, will remove debris from the system. The condenser or heat exchanger should never function as a main filter or screen.

CORROSION RESISTANCE

Corrosion Product Films

The corrosion resistance of copper-nickel alloys in seawater depends upon the nature of the corrosion product film that forms on the surface after it is wetted with water. **Figure 7**(12) shows the rate of film formation on C70600 (copper-nickel alloy compositions are given in **Table 1**) tubing in clean seawater at 16 C in terms of the reduction in copper in the effluent from one minute to three months after startup. Ten minutes after startup, the copper in the

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TABLE 1

Alloy Compositions (Weight Percent)

Element	C70600 Range	C71500 Range	C71640 Range	C72200 Range
Ni	9.0-11.0	29.0-33.0	29.0-32.0	15.0-18.0
Cr	—	—	—	0.3-0.7
Fe	1.0-1.8	0.4-1.0	1.7-2.3	0.5-1.0
Mn	1.0 max	1.0 max	1.5-2.5	1.0 max
Zn	1.0 max	1.0 max	—	—
Pb	0.05 max	0.05 max	0.01 max	—
Si	—	—	—	0.03 max
C	—	—	0.06 max	0.03 max
Ti	—	—	—	0.03 max
S	—	—	0.03 max	—
Cu	Balance	Balance	Balance	Balance

effluent had decreased tenfold, and one hour after startup by one hundredfold. After three months, the film was mature enough so that copper in the effluent was essentially the same as the copper level at the intake. The data in **Figure 8**(13) confirm the increasingly protective nature of the film through 14 years of exposure. This long-term protective nature of the corrosion product film on copper-nickel alloys (C71500 was also included in the 14-year tests yielding a long-term corrosion rate similar to that of C70600(7,14)) is responsible for the 20-plus years' service life of alloy C71500 in shipboard condensers (15) and in many coastal plants.(16)

The normal corrosion product film is thin, adherent and durable. Once fully formed and reasonably mature, the film on copper-nickel alloys will withstand considerable excursions in water velocity, pollution and other conditions normally adverse to the good performance of copper alloy tubing. Good, protective films will form in cold seawater (less than 20 C) but they take considerably longer time to mature.(17) Francis(18) observed at temperatures below 10 C that greater impingement attack was noted on alloy C71500 due to a lack of iron enrichment in the corrosion film. No such change was observed for C70600 nor the higher iron-containing alloy C71640. Corrosion rates and film formation at elevated temperatures were studied by Ross,(19) who observed that high bicarbonate alkalinity is beneficial to the formation of good films on C70600 at a temperature of 60 C. Film formation is retarded or prevented at pH levels below 5 in aerated seawater. Copper-nickel alloys remain resistant to corrosion in deaerated seawater at low pH as has been experienced in numerous distillation type desalination plants.(20)

Velocity Effects

The corrosion rate of copper alloys can be affected by seawater velocity above a certain limit identified for each alloy. The more adherent and protective the "passive" film on a particular alloy, the higher the "breakaway" velocity and the greater its resistance to impingement attack or erosion corrosion. Much information has been published on the effects of high seawater velocity vs. the corrosion of copper-base alloys. The desire to obtain better resistance to impingement attack led to the development of a new copper-base alloy C72200,(21) containing approximately 16% Ni and 0.5% Cr. Results of numerous impingement and erosion corrosion tests of copper, admiralty and aluminum brass, 90-10 and 70-30 copper-nickel, and the chromium-containing copper-nickel alloy yield the industry accepted design velocity limits for condenser tubing shown in **Table 2.**(22) Other tests included alloy C71640, containing 2% Fe and 2% Mn, and would indicate a velocity tolerance much greater than that of alloy C71500 but less than the limit for C72200.(7)

TABLE 2

Accepted Maximum Tubular Design Velocities for Some Copper Alloys

Alloy	Maximum Design Velocity (m/s)
C12200	0.6
C44300	1.2
C68700	2.4
C70600	3.6
C71500	4.6
C72200	>9.0
Minimum velocity to prevent sediment deposition and under deposit corrosion	1.0
Normal design velocity	2.0

Two studies(23,24) were conducted to characterize the behavior of copper-nickel alloys under conditions simulating partial blockage of a condenser tube. In one-year natural seawater tests, enhanced resistance to erosion corrosion was observed for both the C72200 and C71640 alloys as compared to C70600 and C71500. Some localized corrosion (pitting or crevice attack) was noted on the two more highly alloyed materials but not on the standard alloys. This observation was also noted in a summary evaluation of alloying effects on the corrosion of copper-nickel alloys.(25) The tube wall shear stress around a 90% blockage was determined by Sato(26) and approximated the limiting shear stress postulated by Efird(27) for alloy C72200. This was determined with a bulk seawater velocity of only 2 m/s, well within the accepted limits for normal design velocities for tubing. One should remember the earlier discussion of intake systems where proper design and operation should not allow tube blockage to occur.

Although much has been written about the effect of high velocity, much less attention has been given to the extremely damaging effect of low velocities. The authors have undertaken several failure analyses of C70600 tubing only to discover that the original design flow rates were less than 1 m/s (1-1.5 ft/s). At such low flow rates, there is time for even very light mud and sediment loadings to deposit out in the tubing leading to underdeposit corrosion and tube failures. Low flow rates are as damaging (perhaps more so) as high flow rates and should be guarded against in the original design and operation.

Very little information has been published about the flow pattern from the piping to the waterbox or channel head and into the condenser. The authors have encountered a number of instances in which the waterbox, channel section or floating head were simply too small to handle the volume required for the condenser. Severe turbulence and inlet end erosion corrosion resulted. When it is not possible to enlarge the inlet section, it is sometimes possible to install a distribution plate to absorb the turbulence before the water enters the tubing.

Two pipe to waterbox arrangements have given trouble. First, center nozzle type inlets into a shallow waterbox have led to excessive turbulence in the tubing in the center of the tubesheet opposite the inlet pipe and to silting and underdeposit corrosion of flow starved peripheral tubes. Second, side entry nozzles into channel heads have led to excessive turbulence and inlet end erosion corrosion when the nozzles were placed close to the tubesheet. Two guidelines that may be helpful are: 1) allow 10-20% greater volume in the waterbox, channel head or floating head than the tubing will handle; 2) position the center line of the side entry nozzles a full diameter from the tubesheet.

Sand and Silt

The effect of abrasion by sand has been investigated but is difficult to quantify. Sand loadings of less than 200 ppm rarely damage good protective films on copper-nickel alloys. Very fine sand (<0.05 mm) loadings are tolerable up to about 1,000 ppm. Larger diameter and harder sand particles tend to be increasingly abrasive to the film in the 200-1000 ppm range. C71500 has somewhat greater tolerance for sand and C68700, somewhat less. For sand loadings above 1,000 ppm and for larger particle sands in the 200-1,000 ppm range, alloy C71640 has proven very resistant in shallow water estuaries and in shallow water intakes of desalination plants along the Arabian Gulf. Alloy C72200 would be expected to resist sand abrasion quite well also. A good order of most to least resistance is: C71640 > C72200 > C71500 > C70600 > C68700.

Silt or mud has no abrasive effect on the corrosion film, but can be very damaging if allowed to deposit in tubing and remain in place over substantial periods of time. Silt tends to be swept through the tubing when the units are operated near normal design velocities of 2 m/s. At lower velocities, the amount of silt that may be deposited is a function of the settling rate, the actual velocity and the length of the tube. At velocities below 1 m/s, experience has shown that corrosion failures can be expected within 6-12 months unless frequent cleaning is successful in removing deposits before under deposit corrosion initiates.

What is believed to happen in a silt or sediment type deposit is, first, oxygen depletion in the lower part of the deposit next to the tube surface. The upper layer of the deposit remains aerobic with active bacteria. Second, and after the lower layer is depleted in oxygen, sulfate reducing bacteria become increasingly active, generating sulfides. As the sulfide concentration increases, the protective film, already weakened by the absence of oxygen begins to break down and a general pitting type of attack follows. This is now generally referred to as microbiologically influenced corrosion (MIC).(27)

If the deposits are removed and the surface is cleaned before pitting has penetrated the tube wall, the film is easily reformed when clean seawater is reintroduced and the tubing is returned to service. Even if the tube is not clean after silt removal, the film will reform, but it takes a longer time. The remaining service life can be improved by installation of better strainers and by more frequent mechanical cleaning. One of the great strengths of the copper-nickel alloys is their ability to recover from abuse, reform good films and give good continued service.

TABLE 3
Galvanic Couple Data for C70600 and C71500
With Other Materials in 0.6 m/s Flowing Seawater
One Year Exposures - Equal Area Couples

Uncoupled	**Corrosion Rate (µm/y)**
C70600	31
C71500	20
AlBronze (C61400)	43
Carbon Steel	300
Titanium	2
Couples	
C70600	25
Al Bronze (C61400)	43
C70600	3
Carbon Steel	787
C70600	208
Titanium	2
C71500	18
Al Bronze (C61400)	64
C71500	3
Carbon Steel	711
C71500	107
Titanium	2

Galvanic Effects

As a general rule, the copper-base alloys are galvanically compatible with one another in seawater. The copper-nickel alloys are slightly cathodic (noble) to the nickel-free copper-base alloys, but the small differences in corrosion potential generally do not lead to serious galvanic effects between alloys unless unusually adverse anodic/cathodic area ratios are involved.

Corrosion rates for galvanic couples of alloys C70600 and C71500 with other materials are shown in **Table 3.**(7) These data demonstrate the increased attack of less noble carbon steel coupled to copper-nickel alloys, the increased attack on the copper-nickel alloys when coupled to more noble titanium, and the general compatibility of copper-nickel alloys with aluminum bronze. It should be noted that coupling the copper-nickel alloys to less noble materials, such as carbon steel, affords protection to the Copper-nickel. This effectively reduces its corrosion rate, thereby inhibiting the natural resistance to biofouling of the alloy.

Alloy C70600 is very slightly anodic to C71500 and some advantage has been taken of this fact. Alloy C70600 has been used as cladding on a substrate of C71500 for oil coolers. Any local penetrations by turbulent seawater, such as by erosion corrosion, of the C70600 are arrested when the underlying C71500 alloy is reached, until some significant area of the anodic cladding has been consumed. This

TABLE 4

Galvanic Corrosion Data for C70600 Cast Alloy Couples In Seawater *

Alloy	Galvanic Effect ** C70600	Galvanic Effect ** Other Alloy
C70600	1.0	—
cast 90-10 CuNi	0.8	1.6
cast 70-30 CuNi	0.9	1.0
85-5-5-5 (C83600)	0.9	1.5
Monel Bronze (C92200)	0.7	1.8
CN7M Stainless Steel	1.5	0.6
CF8M Stainless Steel	1.2	0.1
Gray Iron	0.1	6.0
Ni-Resist Type I	0.4	2.1
Ni-Resist Type II	0.3	2.6
Ni-Resist Type D2	0.3	2.0

* Seawater velocity: 1.8 m/s
Seawater temperature: 10 C
(Ni-Resist couple tests: 29 C)
Exposure time: 32 days
Equal area couples

**Ratio of mass loss in couple to control

clad construction increased the life of an all C70600 construction in plate type coolers from about six months to more than five years of continuous use.

Results of short-term galvanic couple tests between C70600 and several cast copper-base alloys and ferrous alloys are given in **Table 4**. The corrosion rate of cast 70-30 copper-nickel was unaffected by coupling with an equal area of C70600, while some increased corrosion of other cast copper-base alloys was noted. Corrosion rates of cast stainless steels were reduced with a resultant increase in corrosion of C70600. Gray iron displayed the largest galvanic effect while the corrosion rates of Ni-Resist alloys nominally doubled. Although some caution should be exercised in using absolute values from any short-term tests, the relative degree of acceleration of corrosion from galvanic coupling was shown to be unaffected by extending some tests with Ni-Resist C70600 couples to one year. It should be noted that these short-term tests were conducted in relatively cold seawater at 10 C, although the Ni-Resist couples continued through a full year with an ambient temperature range of 7-30 C.

When addressing the subject of galvanic corrosion, one should not overlook the dissimilar metal couples so often found in the entry area to the heat exchanger, i.e., the waterbox, tubesheet and tubes. Carbon steel waterboxes coated with 100% solid epoxy coatings are fairly standard. Any pinhole, "holiday" or slight mechanical damage that exposes the substrate steel, however, results in a tiny anode of steel coupled to the more noble alloys of the copper family or titanium or stainless steels. Deep corrosion of the steel can be expected at these very adverse cathodic/anodic area ratio points, as shown in **Figure 9**. Corrosion of the exposed steel also undermines, lifts and peels the coating. Loosened coating sections result in further damage in plugging tubes. Generally, cathodic protection via galvanic anodes or an impressed current system is employed to protect coated waterboxes and is advised in the initial design.

The contact between the tubes and tubesheet can lead to galvanic corrosion, particularly if proper attention is not given to materials selection. Key problem material combinations in recent years appear to be in the use of titanium or stainless steel tubing (particularly in retubing existing units) where tubesheets of muntz metal (C63500) or aluminum bronze (C61400) exist.(28) Severe galvanic corrosion of these tubesheets has resulted and led to studies that showed the effective cathodic area was many times larger than had been assumed, approaching a 1,000:1 cathode to anode ratio.(29) These copper alloy tubesheets coupled to titanium or stainless steels require a carefully designed cathodic protection system.(30)

Effects of Pollution

Polluted cooling waters, particularly in coastal harbors and estuaries, have reportedly caused premature failures of power plant and shipboard condenser tubing employing copper-base alloys, including the copper-nickels. Gilbert(31) noted that during the early 1950s, polluted waters were the most important factor contributing to failure of condenser tubes. Though pollution in many harbors has been dramatically reduced by enforcement of strict water quality standards in recent years, accelerated attack of condenser tubes and piping materials by polluted seawater has still been reported.(22)

Attack of copper-base alloys by polluted seawater (generally hydrogen sulfide, or H_2S) has been addressed in numerous test programs.(32-40) The primary sources of the sulfide ion are: 1) the action of sulfate reducing bacteria, under anaerobic conditions (i.e, in mud, silt or sediment deposits), on the natural sulfate present in seawater; 2) the putrefaction of organic sulfur compounds from decaying plant and animal matter within seawater systems during periods of extended shut-down.

Syrett(41) has studied the behavior of alloy C70600 in aerated and sulfide polluted waters. He summarized a great deal of this work in **Figure 10**. In the complete absence of oxygen, corrosion rates were low, as indicated at point 1 and current i2, and remained low up to sulfide concentrations as high as 55 g/m³ and velocities up to 5 m/s. In aerated waters, corrosion rates were somewhat higher, referring to line AB and current i2. The higher corrosion rate in aerated waters is due to the change from hydrogen reduction to oxygen reduction as the primary cathodic reaction. In polluted waters where both oxygen and sulfide may be present under transient conditions, the cathodic reaction is still oxygen reduction with much higher corrosion rate, referring to point 2 and current i4. This work illustrates the high corrosion rates likely to occur in partially deaerated waters with sulfides present and in estuarine waters where there is alternate exposure to aerated waters and partially deaerated waters with each change of tide.

Syrett [41] also found that the thick black sulfide film formed in sulfide polluted waters would be replaced by a normal oxide film in about nine days when the sulfide polluted water was replaced by clean aerated seawater. This ability of poor films to be replaced by good films upon exposure to normal aerated seawater has proven to be one of the primary reasons C70600 alloy tubing has performed so well in ships, many of which are outfitted in polluted harbors.

Todhunter's work[42] with copper-nickel tubed condensers in Los Angeles Harbor also illustrates the longevity of copper-nickel tubing exposed first to sulfide and subsequently to aerated seawater (**Figure 11**). Originally, the 10 condensers were tubed with alloy C68700 which failed due to sulfide pollution. The units were then retubed with C71500 and C70600 in the mid to late 1940s when, as indicated in **Figure 11**, there was still 1-2 ppm H_2S in the harbor waters. As water quality improved after World War II, the original exposure to sulfides was followed by exposure to aerated waters (after 1948). The original sulfide-containing films were replaced by cuprous oxide films and 18 years later Todhunter reported the copper-nickel tubing originally exposed to sulfides was giving excellent service with very low failure rates.

In virtually all published test programs on the effects of sulfide pollution, test specimens were exposed directly to the sulfide-containing water or alternately to the polluted water first and then to clean, aerated seawater. One instance in our own laboratories included initial exposures of C70600 and C71500 specimens to clean seawater for periods up to 4 months, followed by exposure to seawater containing up to 0.5 ppm H_2S. The protective cuprous oxide film formed over four months provided nearly total immunity from attack in the sulfide polluted seawater. This explains the well-known ability of ships at sea to enter polluted harbors for reasonable periods of time without damage to the copper-nickel tubing.

Effects of Dissolved and Non-condensible Gases

Referring to **Figure 2**, gases as well as sediment and larvae pass through the screen and enter the condenser. The gases include O_2, CO_2, NH_3, Cl_2 and in the absence of oxygen, H_2S.

Dissolved **oxygen** is beneficial to good film formation and film maintenance on copper-nickel alloys. Oxygen is also helpful in oxidizing H_2S to reduce or eliminate its effectiveness in corroding copper alloy tubing. Excessive air, however, can be damaging as has occurred on one group of ships fitted with scoop injection. The hull and scoop arrangement was such that so much air entered that many of the tubes in the upper section of the condenser were air blanketed and ineffective. Erosion corrosion at the inlet ends was severe enough to require the use of tube end inserts to protect the inlet end.

Carbon dioxide in amounts normally found in seawater has not proven detrimental to copper-nickel tubing. Excess CO_2 in amounts which would reduce the pH below 5 could be damaging, but such concentrations have seldom, if ever, been encountered in practice.

Ammonia from industrial wastes or animal excrements has been damaging to C68700 and, on rare occasions, to C70600. The effect of ammonia has not been studied to the same extent as the effect of sulfides. Nevertheless, the presence of any significant amount (for instance in the 10-20 ppm range) should be reason for considering field tests or remedial measures.

Effects of Chlorine

Coastal power and process industry plants have used chlorine to control biofouling and slime formation for many years. General experience indicates that Cl_2 concentrations in the range of 0.2-0.5 ppm will control biofouling with no effect on the corrosion of copper-nickel alloys. Results from tests on C71500 for six months are shown in **Figure 12**,[43] indicating no adverse effect on corrosion at seawater velocities up to 3 m/s. In fact, a slight reduction in corrosion rate was noted even at chlorine levels of 1.5 ppm injected intermittently.

Even though alloy C70600 is inherently resistant to attachment of fouling organisms, a few of the larvae which pass through even the smallest screen openings are able to attach to the surface during periods of low flow or shut down. The few that do attach determine the interval between mechanical cleanings needed to restore full heat transfer capability. Without chlorine injection, mechanical cleaning to restore heat transfer may be needed in one or two months. Chlorine injection will extend the interval between mechanical cleanings and maintain original heat transfer capability for extended periods. Chlorine injection is normally provided for heat exchangers in coastal plants which are seldom cleaned more than once a year and for naval ships which must maintain their equipment at maximum efficiency at all times. Chlorine may be added in the gaseous form or developed *in situ* via electrolytic chlorine generation.

Effects of Marine Biofouling

The copper-nickel alloys have long been recognized for their inherent resistance to marine fouling. This resistance is usually associated with macrobiological fouling such as barnacles, mussels and marine invertebrates of corresponding size. Excellent service experience in seawater intake systems including piping, screens, waterboxes, tubesheets and tubing has confirmed much of the research and testing results demonstrating anti-fouling properties. Bulow[44] and LaQue and Clapp[45] demonstrated that fouling was not observed on alloys containing 80% copper or more, and only incipient fouling was noted on C71500. Efird and Anderson[14] later confirmed these observations in exposure tests in clean seawater up to a 14-year duration. Likewise, practical experience with boat hulls of both C70600 and C71500 copper-nickel alloys has demonstrated excellent resistance to hard shell fouling and an accompanying reduction in hull maintenance costs.

Ritter and Suitor(46) studied biofouling growth on titanium and C70600 at 27 C and at various seawater velocities. They observed that the major fouling problem with titanium was silt particles bound by organic growths, that attach at low velocity, while C70600 "fouls" by corrosion products and silt. Increasing velocity removes the silt but not the marine organisms that have attached to titanium. Initial and continuous water velocities above 1 m/s can keep most alloys free of biofouling. The U.S. Navy has reported 47 marine fouling problems can be minimized in titanium condensers or heat exchangers by *always* operating at water velocities in excess of 1.2 m/s throughout the heat exchanger.

Studies by Lewis(48) demonstrated the excellent resistance to biofouling and maintenance of heat transfer efficiency for alloy C70600 in natural seawater. This work, shown in **Figure 13**, indicates the relatively slow rise in heat transfer resistance on the control tube (1-in diameter with seawater flow at 1.8 m/s) until a mechanical brush cleaning was necessary on day 112 of the 180-day test to keep the heat transfer resistance (R_t) below 0.9. By comparison, non-copper alloy tubes were brush cleaned 12 times in 120 days to maintain the same heat transfer. When intermittent chlorine injection at 0.25 ppm for 24 min/day was introduced, the heat transfer resistance had risen only to 0.4 on day 166, at which time a single sponge ball pass reduced the R_t factor by 50%. An important observation in Lewis' work was that carefully monitored and controlled mechanical cleaning of C70600 tubing can maintain excellent heat transfer resistance and corrosion resistance. If mechanical cleaning is utilized, it must be remembered that too great a frequency may remove the protective corrosion film and be detrimental to tubing life.(49)

Ferrous Ion Treatment

It is well established that not only iron in the alloy but also iron additions to the seawater are beneficial in establishing a protective surface film on copper alloys.(50,51) Ferrous ions from either ferrous sulfate or driven iron anodes have been used,(51-52) particularly where sulfide ion pollution has been encountered in cooling waters. Hack and Lee(53) demonstrated that continuous low level addition of ferrous sulfate could counteract accelerated corrosion of alloy C70600, as shown in **Figure 14**. As noted previously, ships at sea employing copper-nickel alloy condensers rarely incur corrosion problems when in port.

Crevice corrosion

Crevice corrosion is rarely observed on copper-nickel alloys but, when detected, is usually metal ion-concentration cell type crevice corrosion. In this mechanism, metal ions accumulate in the occluded area. The crevice becomes ennobled and dissolution occurs adjacent to the crevice at surfaces exposed to aerated seawater. Velocity tends to aggravate this type of corrosion once initiated, although penetration rates are not usually severe. Anderson explained that this type of localized attack on copper-nickel alloys is relatively insensitive to the bold/sheltered area ratio since the area of the cathode is determined by dimensions within the crevice rather than the surface outside the crevice.

Dealloying

Dealloying of copper-nickel alloys is quite rare in clean seawater and only observed at temperatures above 1,000 C under conditions of high heat flux.(54)

Stress Corrosion cracking

The copper-nickel alloys are not susceptible to cracking as has been demonstrated in many distillation-type desalination plants.

MATERIALS SELECTION

Tubing

Condenser and heat exchanger tubing of arsenical admiralty brass predominated the field until aluminum brass was developed for better impingement corrosion resistance. Much research and development in the copper industry during the 1920-1960 period was devoted to development and enhancement of the stable, protective corrosion film on copper-nickel alloys. The net result of this era in terms of today's much used copper-nickel family of alloys is what is now considered the basic tubing alloy of C70600, plus alloys C71500, C71640 and C72200. Where higher water velocities, turbulence and entrained solids are found, the latter three alloys are the logical choice. For instance, in the large tankers and container ships fitted with scoop intakes for their main condensers, water turbulence is a problem that is difficult to control by any means other than the designers' selection of alloy C71640. Much less experience has been obtained with the erosion corrosion resistant alloy C72200, but it remains an interesting development.

In the process industry, C70600 tubes are also the basic choice for heat exchanger tubes where they are compatible with process-side conditions. When not compatible, duplex or bimetallic tubes, of either steel or a specific grade of stainless steel over an internal copper-nickel tube, is sometimes used. These require special heat exchanger design in both rolled and welded tube/tubesheet construction.

A very well-known survey of condenser tube performance in coastal power plants was conducted some 25 years ago,(55) but still stands as an excellent reference today. In both clean and polluted seawater where five different tubing alloys were in service, the calculated failure rate per 10,000 hours of operation was 0.05 to 0.11 for C70600 and 0.004 to 0.060 for C71500. The authors concluded that there was an 85% probability of attaining 20 years life with not more than 5% tube loss for alloy C70600. The probability for C71500 was slightly less at 81%.

This survey also included a report from 20 U.S. Navy Destroyers, all in service for at least 20 years. All tubing was alloy C71500 with C71500 tubesheets in both main and auxiliary condensers. The average failure rate was 0.008 in auxiliary condensers and 0.018 in main condensers.(36)

Tubesheets

Any trend toward welding tubes to the tubesheet and galvanic considerations strongly suggests use of the same alloy for tubesheets as the tubes. Alloy C70600 is a good selection with tubing of the same alloy. Tubesheet alloys should not be more noble than the tubing alloy. Hence, when C71500 or C71640 tubes are utilized, the best tubesheet selection would be C71500.

Bronze tubesheets are still being used, beginning with some old units employing Muntz metal C28000 or the leaded alloy C63500. Aluminum bronze alloy C61400 is also used, but there is some preference for the more corrosion resistant nickel-aluminum bronze alloy C63000. These tubesheet materials are anodic to C70600 and C71500 tubing and provide a small measure of protection to the tube ends.

Solid alloy tubesheets are desirable, although there are some instances in process industry heat exchangers where clad tubesheets may be employed, depending on shell-side requirements. In the case of clad tubesheets, the welded tube to tubesheet joint is recommended for maximum reliability.

Waterboxes

Waterboxes of cast iron or carbon steel with a coating of rubber, plastic or 100% solids epoxy paint are quite commonly found. As mentioned previously in the section on galvanic effects, cathodic protection is strongly recommended to protect the steel at small breaks or pinholes in such coatings.

Thin linings of C70600 have been utilized to cover steel waterboxes. The process of attaching the lining to the steel by MIG spot welding was developed in the U.K.(37) and the British navy has used this process.

For small waterboxes, Ni-Resist cast iron can be used since it has better corrosion resistance than carbon steel or ordinary cast iron, hence a longer life. If left uncoated, however, it will provide galvanic protection to the tube sheets and tube ends. This may be desirable for corrosion resistance but not if the antifouling characteristics of copper-nickel alloys are being relied upon.

Solid C70600 or C71500 waterboxes have been widely used in ships and desalination plants. In some cases, a fabricated construction of carbon steel stiffening on the exterior and copper-nickel on the water side provides an economical design. Cast aluminum bronze or cast nickel-aluminum bronze waterboxes are used and, in most cases are acceptable with copper-nickel tubes and tubesheets.

Start-up/Lay-up Procedures

The extended start-up periods of modern power plants as well as the extended outfitting periods of ships have led to failures of copper alloys where water is left in, or incompletely drained from, the seawater cooling system. Leaving the systems full, partially drained or simply wet, invites putrefaction of seawater which can occur within three to four days.(38) Oxygen is consumed by corrosion and biological oxygen demand, i.e., decay of organic matter found in nearly all natural waters. Bacteria thrive and create local environments that favor microbiologically induced corrosion (MIC). Most failures that have been reported during these start-up periods may well be due to MIC, although usually the failures are considered sulfide type pitting corrosion. The remedy is simply good housekeeping.

If units are to be left full for more than two or three days, pumps should be started once each day to displace the stagnant water with a fresh supply of the natural cooling water.(10) If units are to be down for more than a week, they should be fully drained and blown dry to remove all water in low areas between tubing supports.

CONCLUSIONS

1. The normal film that forms on copper-nickel alloys in aerated seawater becomes mature in about three months at 16 C and becomes increasingly protective with time in service.

2. Once mature, the normal film is quite resistant to polluted waters, velocity excursions and other abuse.

3. Abnormal films that form in polluted waters and under some start-up conditions are less protective and more easily disrupted. These films are replaced by normal films once the units are returned to normal operation in clean waters.

4. The inherent resistance of copper-nickel alloys to biofouling enables units to operate for several months between the mechanical cleanings needed to restore original heat transfer capability. Chlorine injection will extend the intervals between mechanical cleanings to a year or more without detrimental effect on the corrosion resistance of copper-nickel alloys.

5. Intake system design to screen out debris, (sticks, stones, crab claws, sea shells, etc.) that could lodge in and partially block tubes is essential to the good performance of copper-nickel alloy tubes. Failures of tubing downstream of lodgements are really screen failures and must be treated as such in order to prevent recurrence.

6 Low velocity can be as damaging, or perhaps more so, than high velocity. Design velocities of less than 2 m/s are likely to subject tube materials to under deposit corrosion and premature failures.

7. During start-up and standby periods, units that are left full should have water circulated for one hr/day. Units that are drained should be blown dry to remove water left in the bottom of tubing between low spots.

8. Copper-nickel alloys are galvanically compatible with copper alloy tube sheets and waterboxes. Coated waterboxes require supplemental galvanic protection to prevent severe corrosion of the substrate steel that becomes exposed where the coating is damaged. Such units also require chlorine injection as the galvanic protection needed for the waterbox negates the inherent biofouling resistance of copper-nickel.

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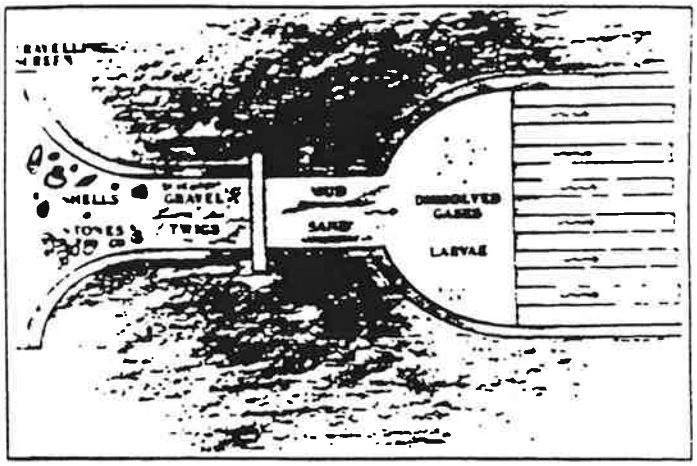

FIGURE 2 Schematic drawing of section of a seawater intake system between the traveling screens and the heat exchanger.

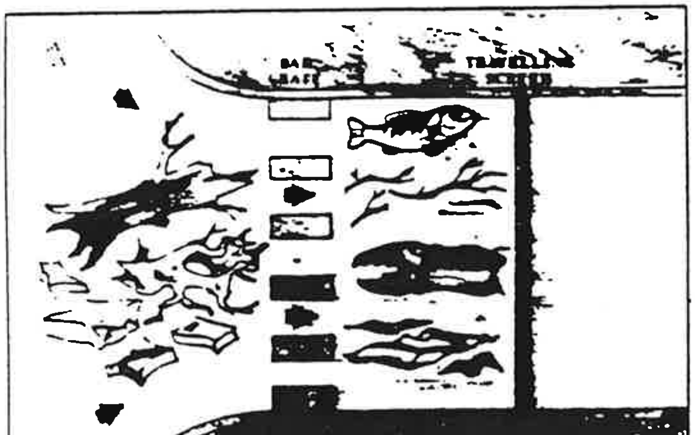

FIGURE 1 Function of the bar grates and traveling screens in a seawater intake system.

FIGURE 3 Two baskets type strainers in a large desalination plant.

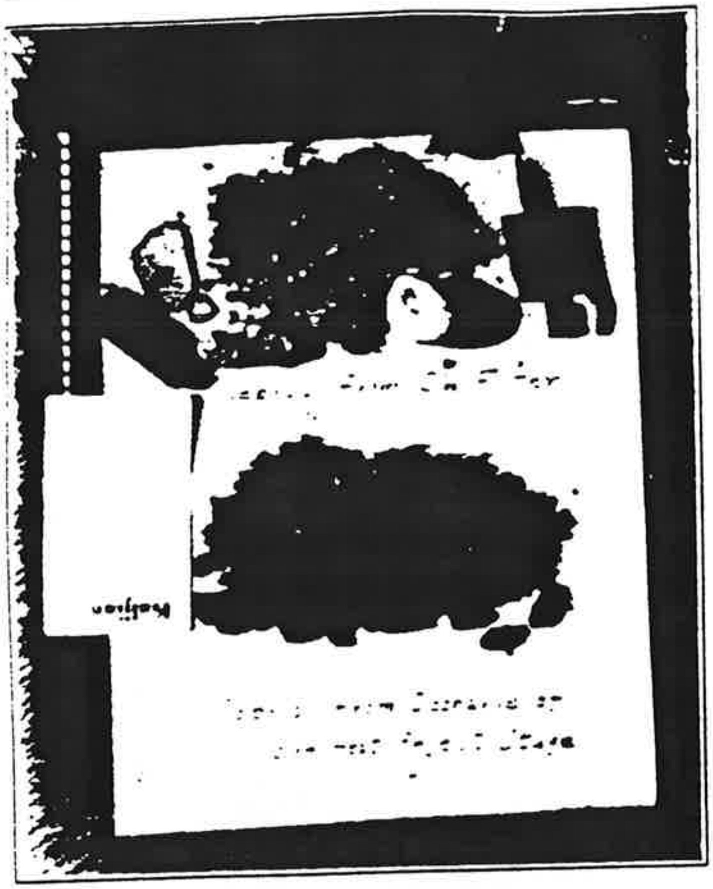

FIGURE 4 Course debris (top) removed from bottom of a strainer in Figure 3; finer debris (bottom) that had passed through the tube bundle.

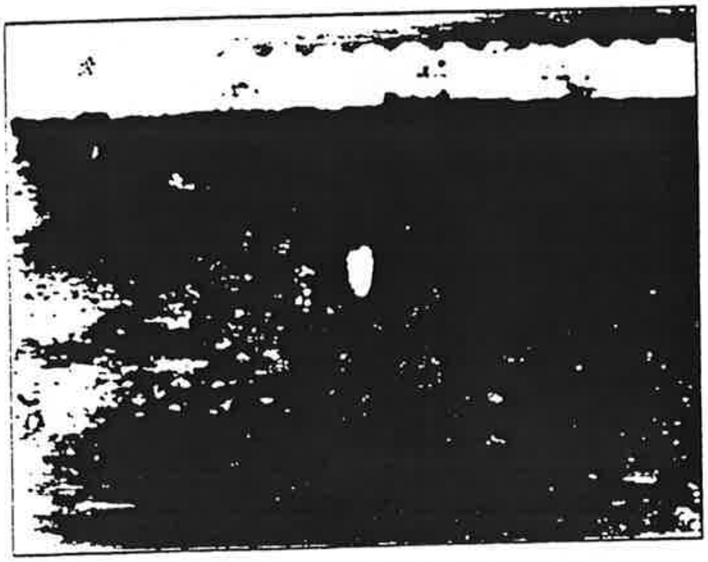

Figure 5 Penetration of tube downstream of lodgement.

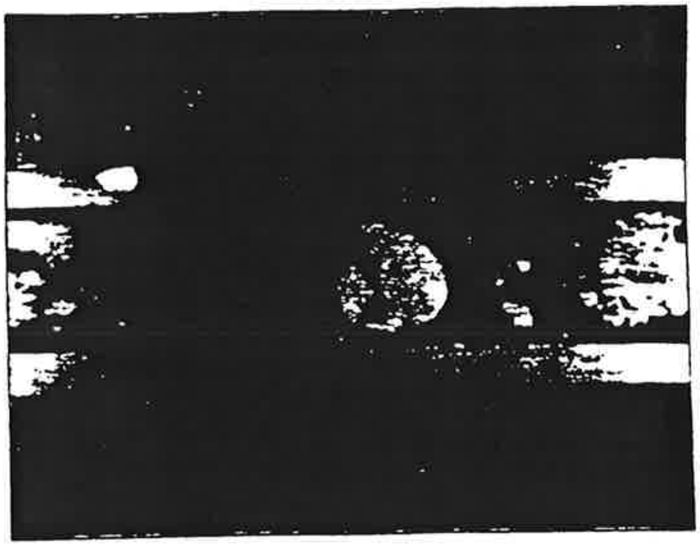

Figure 6 Stone lodged in a tube with hole downstream.

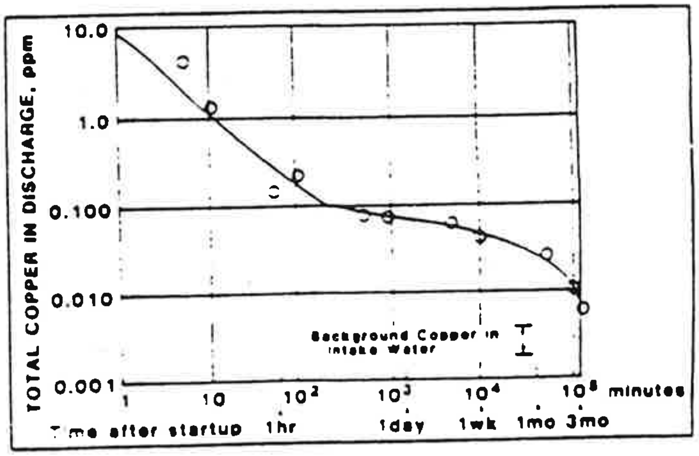

FIGURE 7 Formation rate of corrosion product film on alloy C70600 in seawater.

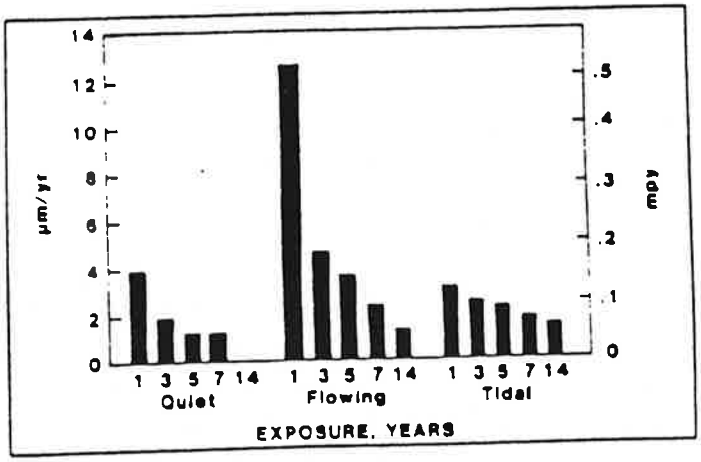

FIGURE 8 Corrosion rates for alloy C70600 in long-term seawater exposures (panel lost from a 14-year exposure in quiet seawater).

FIGURE 9 Corrosion of coated steel waterbox resulting from pinhole failure of coating.

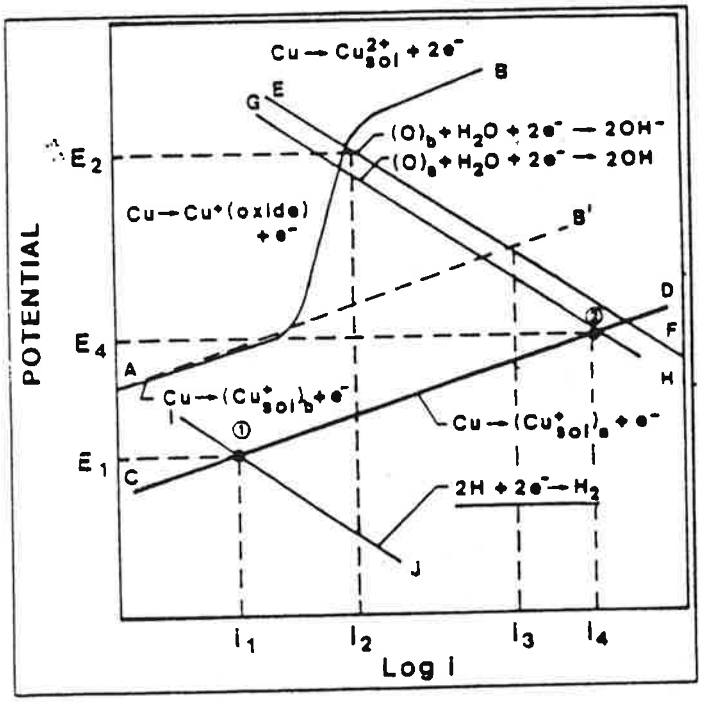

FIGURE 10 Influence of sulfide and oxygen on the corrosion current in a copper-nickel alloy exposed to flowing seawater.

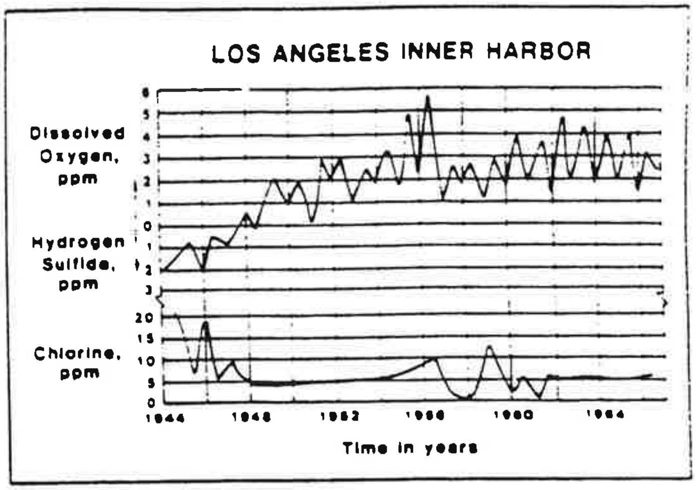

FIGURE 11 Chlorine demand for 0.25 ppm chlorine residual at condenser outlet compared with H_2S and O_2 present in Los Angeles Inner Harbor.

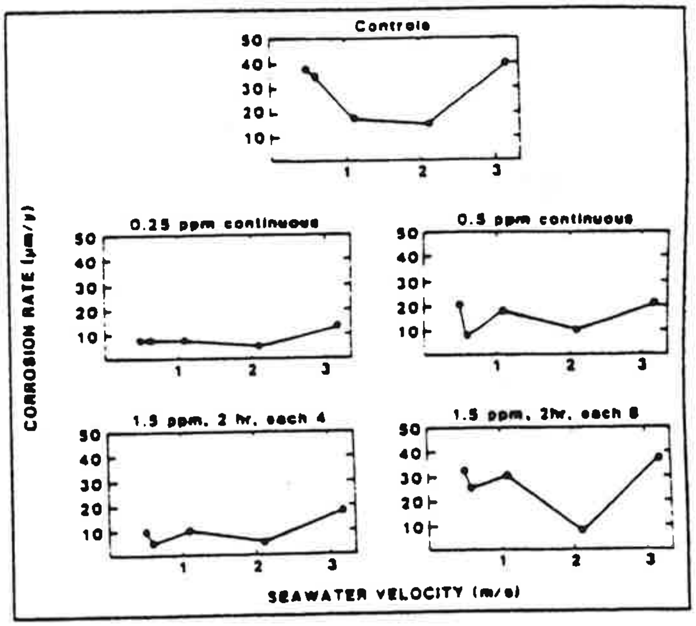

FIGURE 12 Effects of velocity and chlorination on corrosion of 70-30 Copper-Nickel piping in seawater service (187 days test at average seawater temperature of 24C).

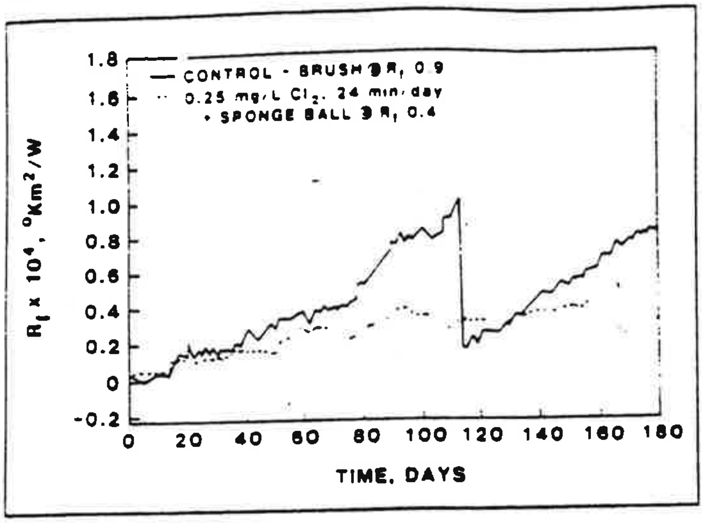

FIGURE 13 Fouling resistance for C70600 tubing with daily intermittent chlorination plus sponge ball cleaning as required to maintain R_f below 0.4 (x 10 -4 km²/W).

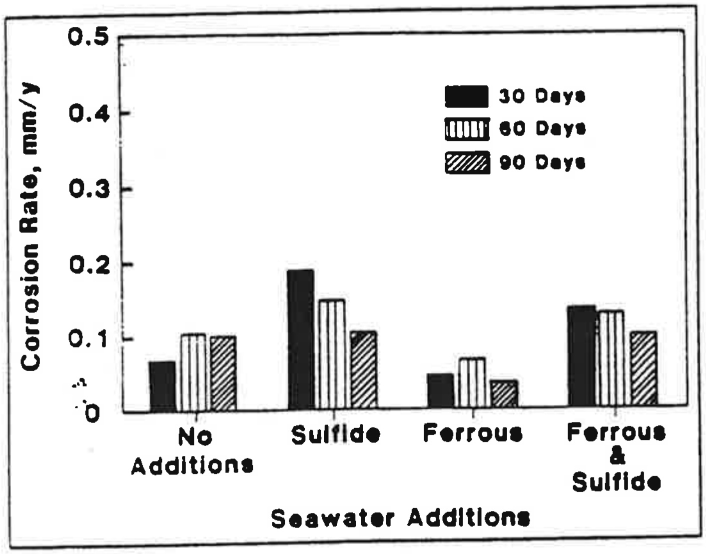

FIGURE 14 Corrosion rates for C70600 exposed to seawater with additions of sulfide (0.05mg/l) and/or ferrous (0.01 mg/l) ions.

COPPER-NICKEL ALLOYS IN DESALINATION SYSTEMS

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INTRODUCTION

Large scale desalination began with the development of the multi-stage flash (MSF) distillation process in the 1960s. Since then the industry has grown rapidly to become a major user of alloy materials, and in particular copper-nickel alloys. Installed capacity worldwide by December 31, 1989 was 13,297,000 m^3/day.(1) Of this, 62% used the MSF process and although the proportion of MSF plants has declined in favor of other processes such as reverse osmosis, it is still favored for large plant capacities such as are required in Middle Eastern countries. The importance of this industry to metal producers can be appreciated from the tonnage of tubing needed to supply the tubing for the installed MSF capacity. This is 210,000 tonnes approximately.

This paper reviews materials requirements for MSF plants and in particular the use of copper-nickel alloys. Although heat exchanger tubing is the most important individual application, there are other important uses such as tubeplate, waterboxes, piping and evaporator shells. The copper-nickels are used for a wider range of components than any other material in MSF evaporators. The requirements of these components will be considered. Also some of the problems which have occurred in MSF plants will be described.

The MSF Process

Figure 1 is a simplified flow diagram of an MSF plant. In this process, evaporation and condensation is split into many stages, thereby increasing efficiency. Incoming seawater is passed through heat exchanger tubing on the exterior of which water vapor, at progressively higher temperatures, is condensing. Finally, it is passed to a heater where steam from an external source supplies the energy for the process and heats the seawater to the maximum process temperature, which depends on the type of anti-scalant used.

The seawater then passes to the evaporator vessel where pressure is released, causing it to boil or flash. This process is repeated in many stages, the pressure being reduced so that flashing occurs at progressively lower temperatures. The condensed vapor is collected and passed down the plant flashing at each stage and is removed at the lowest temperature and is the product from the plant.

In large plants the major part of the seawater stream is recirculated through the plant. Some is blown down to waste and fresh seawater added to maintain concentration within acceptable limits from scaling considerations. This recirculating brine, because it has been boiled many times, is deaerated and this has a marked effect on its corrosivity. In most modern large plants the feed is deaerated in a separate vessel before adding to the recirculating brine.

The final stages in the plant are known as the heat rejection stages and are the only ones exposed to aerated seawater.

Figure 1 is for a plant where the seawater is acidified to control scaling. It includes a decarbonator to remove the carbon dioxide gas resulting from acidification. When polyphosphates or organic anti-scalants are used, a decarbonator is not required.

MSF is basically a heat exchange process and the tubing should have good thermal conductivity as well as corrosion resistance.

HEAT EXCHANGER TUBING

Copper alloys have been traditionally used for handling seawater and this practice was followed when the first large desalination plans were built. The performance of these alloys has, in general, been good and they remain first choice for most plants. **Table 1** gives details of the four alloys used.

The behavior of the alloys listed in **Table 1** in these environments are described in the following paragraphs.

Copper Alloys in Natural Seawater

There is a long and well-documented history of usage of copper base alloys in natural seawater. The most com-

TABLE 1

Alloy	Nominal Composition 5							UNS
	Cu	Zn	Al	Ni	Fe	Mn	As	Number
Aluminium brass.	76	22	2	-	-		0.04	C68700
90-10 CuNi	Rem	-	-	10	1.5	1.0	-	C70600
70-30 CuNi	Rem	-	-	30	0.6	1.0	-	C71500
66-30-2 CuNi	Rem	-	-	30	2.0	2.0	-	C71640

The choice of alloy depends on the corrosion conditions in the different sections of the plant as well as tube costs. The corrosion conditions can be considered as follows:

1. Natural seawater	- Reject section.
2. Deaerated seawater and brine	- Brine Heater and Heat Recovery sections.
3. Incondensable gases and water-vapor	- Tube exterior in all sections.

mon cause of failure in these alloys is by impingement attack or corrosion-erosion, but factors such as sulphide pollution, sand in seawater, chlorination, partial blockage (from faulty screening or marine growth) etc. can be an influence.

A detailed survey of 123 desalination plants was carried out by A.D. Little.(2) The failure rates recorded in this for the reject section were as follows:

	Failure Rates*	Tube Costs
Al Brass	6.8	Least Expensive
90-10 CuNi	2.3	
70-30 CuNi	1.6	
66-30-2-2 CuNiFeMn	0.05	Most Expensive

*Defined as the percentage of tubes plugged and in retubed bundles.

These data agree with the general experience of these alloys in seawater applications. As the survey covered a large number of plants in many locations it is a reflection of the resistance of the alloys to the many factors given above which influence these alloys in seawater. Sato and Nagata(3) compared aluminium brass and 90-10 copper-nickel under conditions of partial blockage, chlorination, and sponge ball cleaning. They showed that the 90-10 copper-nickel was more resistant except with sponge ball cleaning, which should be restricted with that alloy.

In terms of tube costs, the most resistant alloys are the most expensive. For this reason all the alloys listed are used for heat rejection tubing. The 66-30-2-2 copper-nickel is often used in large plants and is preferred to the 70-30 copper-nickel which is rarely used in reject sections. For small and medium-sized plants, 90-10 copper-nickel is normally chosen.

Copper Alloys In Deaerated Seawater and Brine

As corrosion of copper alloys in waters of neutral pH requires the presence of oxygen to enable the cathodic reaction to occur, it could be predicted that deaerated seawater and brine would be less corrosive than natural seawater, data from the A.D Little survey support this view. These data are as follows:

Failure Rates* in Heat Recovery Tubing

Aluminum Brass	1.07
90-10 CuNi	0.38
70-30 CuNi	0
66-30-2-2	0.02

* Defined as the percentage of tubes plugged and in retubed bundles.

Various studies of corrosion under deaerated conditions have been carried out. Anderson(4) confirmed the beneficial effects of deaeration and found that corrosion-erosion effects could occur at intermediate temperatures even at low (40 ppb) oxygen contents. A study by Dow carried out for the OWRT(5) showed that at low oxygen levels all the alloys tested showed high resistance to corrosion. Important differences occurred when the oxygen level increased. **Figure 2** illustrates this effect for aluminium brass, 90-10 and 70-30 copper-nickel. This indicates that aluminium brass is more sensitive to variations in oxygen content which can occur during plant operation.

Another factor which has to be considered is the effect of pH. Although a low pH will not itself cause corrosion of copper alloys, it can by damaging protective films allow the oxygen present to cause corrosion. Evidence for this can again be seen in the data from the A.D. Little Survey, as follows:

Failure Rates* with Acid and Additive Anti-scalants Heat Recovery Section

	Acid	Additive
Aluminum Brass	9.0	0.02
90-10 CuNi	0.36	0.60
70-30 CuNi	0	0

* Defined as the percentage of tubes plugged and in retubed bundles.

As the normal operating conditions, in terms of pH, for acid and additive dosed plants is very similar, the differences in failure rate can only be due to operating outside the design values which is possible with acid dosing. Again, the copper-nickels are more consistent in performance under fluctuating plant conditions.

Another section of the plant which is exposed to deaerated conditions is the brine heater. This section is exposed to the highest plant temperature – up to 120 C. Experience has shown that the tubing in this section has the highest failure rates but when the tubes are examined they are seen to have failed by scaling or due to damage during mechanical descaling; corrosion failures are rare. For this reason it is usual to fit 70-30 copper-nickel tubing in this section because of its higher strength and ability to withstand mechanical descaling. In some cases the reason for failures has been misinterpreted and thin-wall titanium was fitted which resulted in a shorter life than the original copper alloy.

Copper Alloys In Incondensable Gases

The gases evolved from flashing brine pass into the vapor space, are guided to the gas extraction zone by baffle plates, and the concentrated gases are then removed by steam ejectors. These gases are mainly carbon dioxide and air (oxygen and nitrogen). In acid-dosed plants most of the carbon dioxide is removed before the seawater is fed to the plant, but in additive-dosed plants, the heat of the process decomposes bicarbonates and much greater amounts of carbon dioxide are evolved. Seawater normally contains a small amount of ammonia, and this also passes to the vapor space increasing the corrosivity of the gases. Some designers vent the Brine Heater into Stage 1, and if ammonia-forming compounds, such as hydrazine, are used for boiler water treatment, this markedly increases the ammonia content of the gases in the vapor space. Although this ammonia is not a problem in the Brine Heater, as oxygen is absent, it can cause serious corrosion on the copper tubing in the high temperature stages where some oxygen is normally present.

Although there have been some reports of corrosion on tube exteriors in gas extraction zones (Sato and Nagata(6)), the main problem encountered is an increase in copper content in the product water. In one case known to the author this increased to 2.5 ppm, whereas in most plants, it is less than 0.02 ppm.

There is little information on gas concentrations in vapor spaces. Conventional thinking is that most gas is removed in the first few high temperature stages. However recent(7) work on corrosion of carbon steel in MSF plants shows that air inleakage, together with gases cascading down the plant and from flashing distillate, can cause severe corrosion.

Experience from power plant condensers is that 70-30 copper-nickel is the best copper base alloy for resisting corrosion in the gas extraction zone. This alloy is often used for his section even when the unit is tubed with another alloy.(8) Tests in ammonia/carbonate mixtures(9) demonstrated the superiority of 70-30 copper-nickel in these environments. Data from these tests are as follows:

Corrosion in 500 ppm/1,400 ppm NH3/NH4CO3 Solution

Alloy	Corrosion Rate (mm/yr)
Aluminum Brass	0.13
90-10 CuNi	0.10
70-30 CuNi	0.08

In MSF plants 70-30 copper-nickel is often selected for the top temperature recovery stages, especially when additive anti-scalants are used, in order to resist the high concentrations of carbon dioxide and other gases in these stages. As aluminium brass can suffer stress corrosion cracking(2) due to ammonia in incondensable gases, this alloy is not normally used in the high temperature stages although sometimes used in the low temperature recovery stages.

Where vapor-side corrosion occurs, it causes uniform thinning of the tube wall, eventually resulting in perforation. There may be some pitting associated with the thinning but this is normally very shallow and does not cause penetration. Vapor-side corrosion is most frequently experienced in vent condensers where incondensable gases removed from the plant are cooled before exhausting to atmosphere. In these units the life of copper alloy tubing is short – a few years – and titanium or high alloy stainless steel is used.

Heat Exchanger Tubing – Trends In Materials Selection

Based on the considerations reviewed above the optimum materials selection for copper-base alloys would be:

	Preferred Alloy	Alternatives
Heat Reject	66-30-2-2 CuNiFeMn	70-30 CuNi 90-10 CuNi Aluminum Brass
Heat Recovery	70-30 CuNi (Top stages) 90-10 CuNi	90-10 CuNi Aluminum Brass
Brine Heater	70-30 CuNi	90-10 CuNi

Some plants using 66-30-2-2 CuNiFeMn in the reject sections also use this alloy in the Brine Heater and the high temperature recovery stages. Although this is technically satisfactory, this alloy is a little more expensive than the 70-30 copper-nickel, which is preferred.

TUBEPLATES

The normal method of fitting tubes into MSF plant is by roller expanding into tube plates. These plates are subjected to corrosion conditions similar to the tubing and are made from similar copper-based alloys. However, as these plates are relatively thick, as compared to the tubing, sometimes other less expensive alloys are used. **Table 2** gives details of some tubeplate materials often used in desalination plants.

When copper-nickel tubing is used, 90-10 copper-nickel is the preferred tubeplate material. Aluminium bronze is less expensive than 90-10 copper-nickel and has higher mechanical properties (which can be advantageous by allowing a reduction in plate thickness); hence, its use in this application.

Naval brass is the least expensive of the alloys listed but is less corrosion resistant than the others. In natural seawater it can suffer dezincification, despite its tin content

TABLE 2

Alloy (UNS Number)	Tubeplate Materials-Nominal Composition (%)					
	Cu	Ni	Al	Fe	Zn	Sn
90-10 CuNi (C 70600)	REM.	10	-	1.5	-	-
Aluminum Bronze (C 61400)	REM.	-	7	3	-	-
Naval Brass (C 46400)	REM.	-	-	-	39	1

to limit this; but, this can be controlled by fitting iron anodes in the waterboxes.

90-10 copper-nickel and aluminium bronze have good weldability and can be welded directly to the steel shell which simplifies construction. Naval brass can be welded only with great difficulty and is usually bolted to the shell.

90-10 copper-nickel is available as clad plate, i.e., a steel plate with an integrally bonded layer of copper-nickel. Where this is used with roller expanded tubing, an adequate layer of alloy must be provided in order to achieve a tight connection. This layer should be 8-10 mm thick, which means that this type of tubeplate is economical only for thick constructions. A thinner layer is possible if the tubes are welded into the tubeplate, but this is not normally used for MSF plants.

If an inadequate alloy layer is used and a leaking tube to tubeplate joint results, corrosion can occur on the carbon steel behind the alloy layer. This results in the development of a large pit or hole in the steel, and the corrosion product diffuses to the tubeplate surface along the leaking joint. On this surface, a large tubercule of rust forms. In aerated seawater this is mainly ferric oxide, but in deaearated conditions it is usually black magnetic iron oxide. The early stages of this type of corrosion show themselves by evidence of red or black iron oxides "bleeding" from the expanded joint. Cleaning off and re-expanding can sometimes prevent further corrosion.

WATERBOXES

MSF plants require waterboxes and, in cross-tube plants, the number required can be large. Because of the large area of copper base alloy provided by the tubes and tubeplates, galvanic corrosion can occur if carbon steel is used for the waterboxes. Coatings have proven unreliable, with the exception of thick (3-5 mm) rubber linings which are sometimes used in the reject section. Damage to coatings can result in concentration of attack at the damaged area resulting in rapid penetration. Also coating breakdown has resulted in partial blockage of the tubes giving local turbulence and tube failure.

Most large modern plants use waterboxes made from 90-10 copper-nickel clad steel plate. The alloy layer is usually 2.5-3.0 mm thick. This thickness is set by fabrication considerations – the ability to work with tolerances within the thickness of the alloy layer. Corrosion considerations would allow a thickness of about 1 mm which is adequate for the tubing.

90-10 copper-nickel has good weldability. Inert gas welding is preferred, although coated manual electrodes are available. In both cases, the filler material is usually 70-30 copper-nickel to ensure that the less homogeneous cast structure of the weld matches the corrosion resistance of the wrought base material. The filler metals and electrode coatings must contain small amounts of elements with a high affinity for oxygen and nitrogen. These are usually manganese and titanium. Full details of welding these alloys, including clad products, are given in **Reference 10.**

Figure 3 illustrates a technique which has been used to line components with 90-10 copper-nickel. This involves the use of metal inert gas welding to provide a spot weld to fasten the lining to the steel component. **Reference 11** gives details of this technique which has been used for lining waterboxes and other MSF plant components. Thin sheet 1.2 mm is used for waterboxes.

EVAPORTOR SHELLS AND FLASH CHAMBER LININGS

90-10 copper-nickel has been used for construction of evaporator shells – usually in small plants up to 1,000 tonnes/day. It has also been used for lining large plants, notably the 50 mgd Al Khobar plant in Saudi Arabia where all stages are lined with alloy. In this case, 90-10 copper-nickel clad plate was used for the shell with solid alloy for internal components.

In small plants advantage is taken of the ability to weld copper-nickel direct to carbon steel by using relatively thin copper-nickel for the parts exposed to corrosion and providing strength with external steel sections. This gives an economically attractive, high quality construction which has been proven over many years of service life. **Figure** 4(12) shows a plant which operated in Ascension Island for over 20 years. The 90-10 copper-nickel evaporator body, waterboxes, etc., were in excellent condition with no evidence of corrosion damage.

In large plants, corrosion of steel in flash chambers has been a serious problem,(13) and most plants are now partially – sometimes completely – lined with alloy material. Although it is accepted that plants with alloy linings are more reliable and require less maintenance, the economic aspects are often questioned. A study(14) on this aspect concluded that a plant completely lined with 90-10 copper-nickel would cost only 5% more than an unlined one. If this is true for all plants, then the use of linings must be economic.

The choice of lining materials is between stainless steel and 90-10 copper-nickel. Although both are technically satisfactory, the stainless steel is slightly less expensive. However, this saving is offset by the extra care needed to avoid pitting during shutdowns when oxygen has access to the plant. Both materials, therefore, can be accepted for large plants, and both are specified.

Paint coatings have been tried in an attempt to provide a less expensive lining. These have not been satisfactory as the paint film is damaged by the equipment which has to be used inside these plants for routine maintenance. Repair to the coatings is often difficult to fit into the shutdown schedule, and pitting at damaged areas usually results. In some cases breakdown of paint coatings has resulted in blockage of pump filters, necessitating unscheduled plant shutdown for cleaning.

PIPING SYSTEMS

Large amounts of piping are required in MSF plants to carry seawater, brine, etc. Various materials, including steel, coated steel, 316L stainless steel, FRP and 90-10 copper-nickel are used for these pipes. While steel is cheap in first cost, it suffers from corrosion and requires maintenance and replacement. In seawater, 316L stainless steel suffers pitting and, although it can be used in deaerated seawater and brine, care is needed during shutdowns to avoid leaving chloride-containing water with access to oxygen. Coated steel is unreliable and FRP has given problems.(15)

90-10 copper-nickel has been used for piping systems for many years. It is technically suitable for use in both aerated and deaerated seawater and brine, but its economic suitability is sometimes questioned. In this connection, a UK study(16) which carefully examined all factors influencing pipe costs (design, fabrication, installation etc.), is of value. This showed that the installed cost of a ship's seawater system in 90-10 copper-nickel was only 30% more expensive than a system in cast iron and steel, even though the material costs for the alloy system was three times that of the steel system. As the steel system would require renewal at least once in the life of the ship, then the alloy system was clearly more economic.

Considerations similar to those used in the above study(16) apply to MSF piping and to 90-10 copper-nickel piping systems which are widely used in these plants and have performed well. These considerations include good weldability, ability to use high flow velocities (minimizing pipe size and cost), and ready availability of standard pipe fittings.

CONCLUSION

The copper-nickel alloys have a combination of properties, such as corrosion resistance, fabricability and mechanical properties which meet the needs of MSF plants. These alloys, particularly 90-10 copper-nickel, have been used for a wider range of applications than any other material. Also, their performance in these applications has generally been good. Further development of this industry is likely to involve more use of these alloys even when new processes are used. This is because seawater is likely to be the main feedstock for desalination and the copper-nickels have a proven record for handling seawater.

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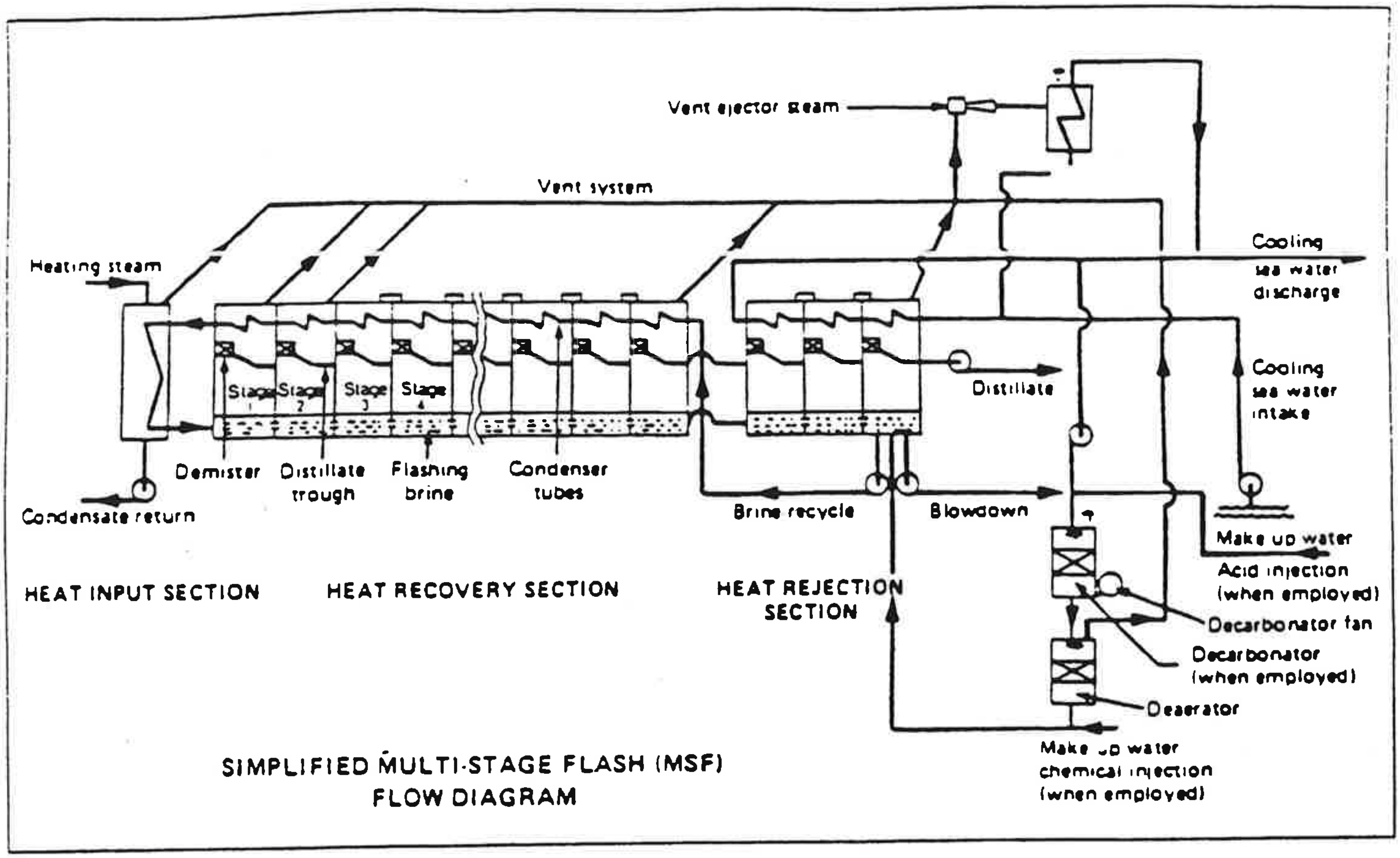

Figure 1 Simplified MFS Flow Diargam

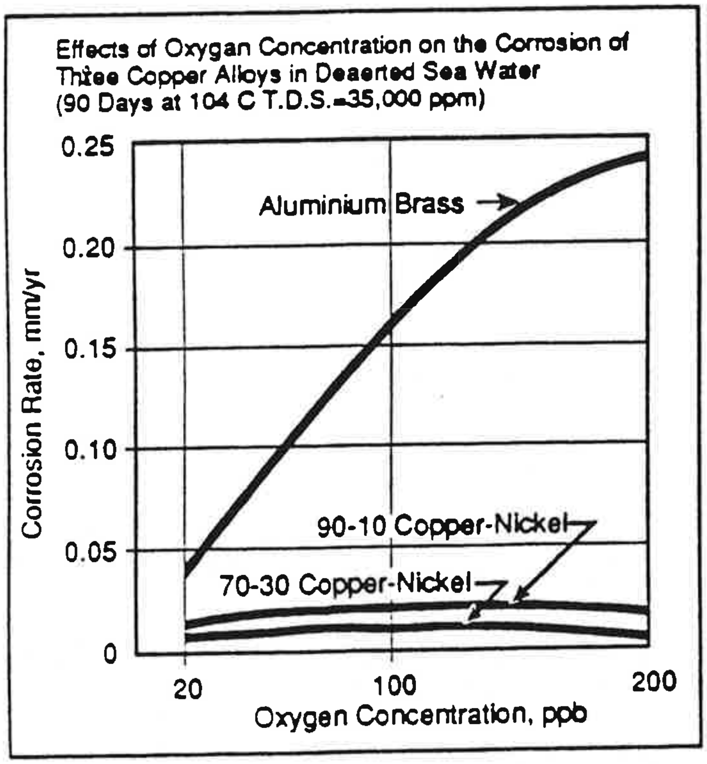

Figure 2 Copper Alloys in Deaerated Seawater

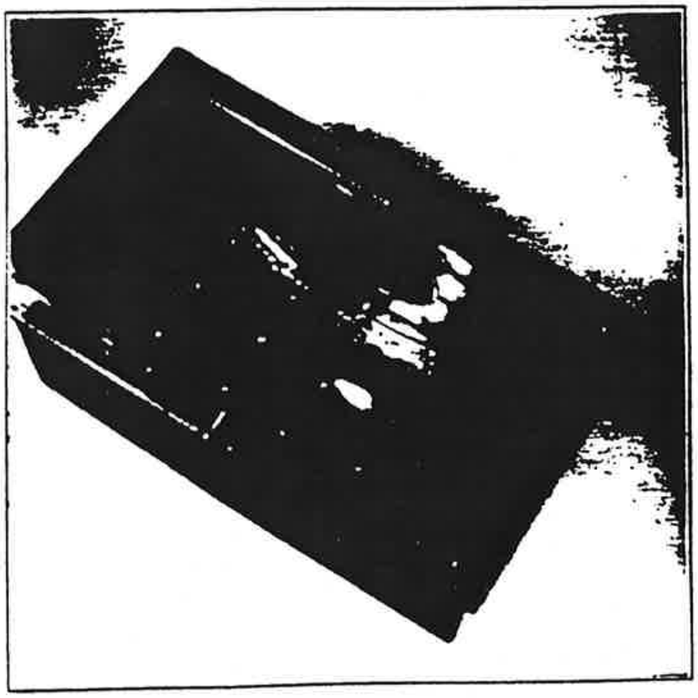

Figure 3 Model Waterbox Lined with 90-10 Copper-Nickel

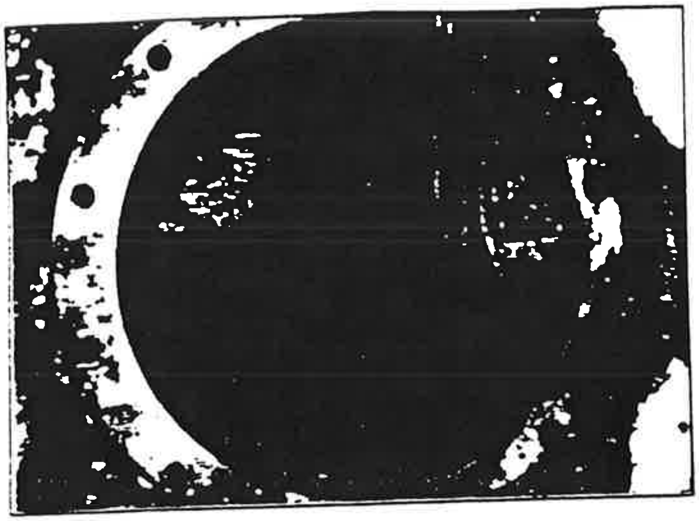

Figure 4 Sharp Edges on 90-10 Copper -Nickel MSF Plant interior after 20 years of service

A REVIEW OF COPPER-NICKEL ALLOY SHEATHING OF SHIP HULLS AND OFFSHORE STRUCTURES

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SHIP HULL SHEATHING

Background

Marine engineers have sought effective and economical means to protect ship hulls and marine structures from the ravages of seawater and marine life for centuries. Wooden hulled ships were sheathed with lead by tramp coastal traders in the time of Alexander the Great. Lead, like copper, resists biofouling growth.

The British Admiralty used sheets of copper nailed to wooden ships starting with the frigate *Alarm* in 1761 to protect against worms and fouling. Galvanic corrosion of iron fasteners and bolts led to loss of the copper and weakening of the ships. It was not until the 1780s with the introduction of copper fasteners that copper sheathing became popular. With the advent of steel hulls, copper sheathing gave way to copper-base antifouling paints.

The ideal hull material for ships of various sizes and duties has been the subject of intense study, and a variety of hull materials are being used or have been evaluated. Copper-nickel as a hull material was first used as early as 1941 in construction of *Miss Revere*, a 13.7 m yacht with a 2mm thick copper-nickel hull. In the mid-1960s, a professor at the University of Alabama designed the yacht, the *Asperida*. He had been seeking material with the best combination of corrosion and biofouling resistance. Alloy C71500, 70-30 copper-nickel, was selected over C70600 90-10 copper-nickel, because the greater strength was an advantage in his particular design.

This led directly to a series of engineering studies by the International Copper Research Association (INCRA) now the International Copper Association), the International Nickel Company and the Copper Development Association Inc. and the construction in 1971 of *Copper Mariner*, a 20.4-m commercial shrimp trawler with a copper-nickel hull. The primary objective was to determine whether the inherent resistance of alloy C70600 to biofouling and corrosion would generate sufficient fuel and maintenance savings to justify the cost premium for the copper-nickel hull.

Copper Mariner (**Figure 1**) has been described elsewhere(2) and will not be elaborated on here. This trawler has a 6-mm thick alloy C70600 hull welded to steel framing. *Copper Mariner* demonstrated a return on investment in the range of 12.9 to 16.7 percent after taxes for shrimp trawler operations off the coast of Nicaragua. These figures are based on measured fuel and maintenance savings and estimates of the increased earnings potential of this boat due to additional days of availability when compared to the sister steel hulled boats.

The corrosion rate of the hull was less than the 0.00125 mm/yr reported for long-term exposure of C70600.(3) Interestingly, hull plate thickness measurements after 52 months of service showed no differences in metal loss in the heat affected zone areas of the hull where re-solution of the precipitated iron had taken place compared to the hot-rolled plate with iron precipitated. The majority of the hull had a dark-colored corrosion product film; the heat affected zones were a light golden color. The speed of *Copper Mariner* is in the 4-10 knot range.

The copper-nickel hull of *Copper Mariner* is very resistant to fouling (**Figure 2**). Comparison with the steel hull of the sister ship just prior to its third cleaning after 18 months of service, is striking (**Figure 3**).

Copper Mariner is 20 years old this year. She is still in service, and at last word from the Minister of the National Fishing Industry in Nicaragua, the copper-nickel hull has never required maintenance. Inspection of the hull at drydockings for propeller and shafting maintenance have shown no noteworthy signs of general or pitting corrosion. Four similar boats with 4.8-mm thick C70600 alloy hulls were built in the early 1970s for service in Sri Lanka.

A number of very successful copper-nickel hull ships have been constructed using a composite material of 90-10 copper-nickel alloy clad on to steel. A second shrimp trawler, *Copper Mariner II*, was built in 1976 with 8-mm, 25% C70600 alloy clad steel hull plate. This hull demonstrated fabricability and weldability using clad material and welding techniques described by Prager, et. al.(4) More recently, the Italian Ministry of the Interior purchased several fire boats for the port at Naples and other locations. These boats have hulls made from 2 mm of 90-10 copper-nickel clad on 6 mm of steel with a length of 22.56 m and a displacement of 72 tonnes. These copper-nickel hulls assure maximum availability of the fire boats by eliminating the need for hull maintenance of any kind.

Two clad-metal-hull pilot boats were constructed in 1987 for the Board of Navigation in Finland. These two boats were planned as a comparison between austenitic stainless steel and 90-10 copper-nickel for use in the Baltic Sea where ice is a major problem. Both boats are reported to be performing well.

Two boats of note have been constructed in Japan. Although we have no details, we were informed of a yacht, the *Akitsushima*, built by the Furukama Electric Co., Ltd., with a 4-mm thick copper-nickel sheath welded to the steel hull. In 1989, this boat was reported to have crossed the Pacific Ocean to Victoria, British Columbia, Canada. The NKK Corporation has reported the construction of an experimental ship, *Cupro*, with a copper-nickel clad steel hull. These Japanese ships are of great interest and we would be most interested in knowing about their performance and construction details. A summary of vessels constructed to date with copper-nickel hulls is presented in **Table 1**. The concept has attracted considerable attention for smaller commercial craft, but a ship of length greater than 25 m has not been built.

Cladding and Sheathing

For larger ships, solid copper-nickel hulls are obviously impractical. Practical means of facing the steel with copper-nickel include both cladding and sheathing. By cladding we mean a composite material having a metallurgical bond between the steel and the copper-nickel alloy. Both hot-roll bonding and explosive forming have been used to produce this metallurgically sound interface. Sheathing refers to the attachment of relatively thin copper-nickel sheet to the hull by welding or the use of adhesives. Sheathing is therefore applicable to ratiofitting existing ships as well as to new construction. Sheathing, with or without an insulating layer between the copper-nickel and the steel, is also applicable to off-shore oil and gas structures as well as a wide variety of bridge, dock structures and power or chemical plant seawater intake systems for corrosion protection and prevention of biofouling. Sheathing with copper-nickel is the main thrust of this paper because of its apparent relatively attractive economics and its flexibility and applicability to a wide variety of marine structures in addition to ship hulls.

As noted at the outset of this paper, sheathing is an old concept. Copper-nickel as a ship hull material, as verified in the experiences of the many smaller craft built to date, does, as has been claimed, provide corrosion protection and eliminate fouling of the hull, both of which contribute to reduced maintainence and fuel requirements. But these concepts have not yet been combined on a large ocean-going vessel to effect the advantages observed when the concept is applied to smaller craft. This may be because a variety of technical and economic issues remain unresolved in the minds of members of the ship building community.

TABLE 1

Vessels Constructed with Copper-Nickel Hulls

Vessel	Hull Length (m)	Launched	Built	Thickness (mm)	Operating
Miss Revere	13.7	1941	USA	2	——
Asperida II	16	1968	Holland	4	USA
Ilona	16	1968	Holland	4	Curacao
Copper Mariner	22	1971	Mexico	6	Nicaragua
Pink Lotus	17	1975	Mexico	4	Sri Lanka
Pink Jasmine	17	1975	Mexico	4	Sri Lanka
Pink Rose	17	1975	Mexico	4	Sri Lanka
Pink Orchid	17	1975	Mexico	4	Sri Lanka
Copper Mariner II	25	1977	Mexico	6+2*	Nicaragua
Sieglinde Marie	21	1978	UK	6	UK/Caribbean
Pretty Penny	10	1979	UK	3	UK
Sabatino Bocchetto	21.5	1984	Italy	6+2*	Italy
Romano Rosati	21.5	1984	Italy	6+2*	Italy
Aldo Filippini	21.5	1987	Italy	6+2*	Italy
Fire Boat VF544	21.5	1987	Italy	6+2*	Italy
Pilot Boat	14.4	1988	Finland	7+2.5*	Baltic
Akitswushima	NA	1989	Japan	steel+ 4**	Japan
Cupro	NA	1991	NKK Japan	4.5+1.5*	Asano Dockyard

* Copper-nickel clad steel plate
** Copper-nickel sheathed steel hull
NA=Not available

We will examine two issues relating to corrosion behavior of copper-nickel ship hulls which are frequently raised, namely the erosion-corrosion capability of the copper-nickel alloys and the likely consequences of the galvanic corrosion of the steel hull in the event of damage to the sheath. The more complex issue of the life-cycle economics of sheathing will be analyzed for a particular ship. Results of a study of sheathing methods and costs for large ships is reviewed.

SEA SERVICE EVALUATIONS

Erosion-Corrosion of Copper-Nickel and the Question of Velocity Limitation

Copper Mariner and many of the other ships listed in **Table 1** have maximum velocities in the range of 10-12 knots (5-6 m/s). Certainly, alloy C70600 has demonstrated excellent corrosion resistance both to pitting and to erosion-corrosion in seawater at these velocities on the hulls of these ships. It remained to be demonstrated that alloy C70600 had adequate tolerance at velocities in the range of 25 knots (12.5 m/s) required of large tankers or freighters. Although the maximum velocity recommended for 100 mm and larger pipe is 3.5 m/s, there was indication that the corrosion rate in pipes of very large diameter, or on the essentially flat plate geometry of a ship's hull, might be quite acceptable at very much higher velocities.

Experiments on large ships were performed to try to directly assess this velocity effect.(5) First, a complete rudder was sheathed and installed on the *Great Land*, a 24-knot roll-on/roll-off vessel. The rudder area is a region of complex and turbulent flow. The tests show that alloy C70600 and the Cu-Ni-Cr alloy C72200 are extremely durable even in the conditions of Cook Inlet off the coast of Alaska, where ice and abrasive silt in the water are encountered. The rudder with 74 m² of copper-nickel alloy sheathing is shown in **Figure 4.**

Corrosion rates were determined by measuring sheathing thickness at intervals of several months up to 14 months of service. Thickness losses were very much a function of position on the rudder as would be expected, but in no position did the thickness reduction exceed 0.1 mm over the 14-month test period. More importantly, the mean loss rate was observed to decrease with time as shown in **Figure 5**. Mean corrosion rates of less than 0.025 mm/yr at the 14-month point were experienced for both alloys. This means that a stable protective film was being formed on the rudder sheathing preventing the potentially disastrous high corrosion rates thought possible by some people in this high velocity, turbulent regime.

Since galvanic interaction between the hull of the *Great Land* and its sheathed rudder may have affected the corrosion results, tests were next performed with copper-nickel panels attached to, but electrically insulated from, the hull and the rudder. Panels with exposed faces 250 mm x 125 mm and insulated with Teflon and epoxy (**Figure 6**) were assembled and fastened to the ship at four locations 4.6 m below the water line. Measurements indicated that some of the panels developed partial grounding to the hull, meaning that in these cases the absolute value of the corrosion rate is probably lower than it would have been had the insulation remained undamaged. The results obtained by thickness measurements showed no significant difference in the corrosion rate of the panels at the various hull locations. The rudder panels exhibited higher erosion-corrosion rates than those on the hull (less than a factor of 2 and the rates were higher on the insulated rudder panels than on the corresponding sheathed-rudder test locations. Cathodic protection of the sheathed rudder by the hull had suppressed the corrosion rate by about a factor of three as shown here:

	Loss Rate (mm/yr)	
Alloy	**Sheathed Rudder**	**Insulated Panels on Rudder**
C70600	0.02	0.08
C72200	0.04	0.10

The C72200 Cr-containing alloy consistently showed slightly higher corrosion rates. This was not as expected and it is not certain that the observed difference is significant.

The corrosion rate data for the insulated panels showed a definite decreasing tendency with time, again indicating that a stable protective film was forming over the 14-month period of the tests. The rates were tending to values of 0.02 to 0.1 mm/yr (and presumably lower if measurements after longer exposure times had been possible), which would be quite acceptable in this application. Based on these observations, it is believed that 12.5 m/s (24 knots) is below the breakaway velocity for copper-nickel in ship hull situations. It is noted that the breakaway velocity determined by jet impingement testing in the laboratory for alloy C70600 was approximately 5 m/s (10 knots). It is possible that the differences in laboratory and ship hull results can be attributed to factors such as:

1. Intermittent flow on a ship hull versus continuous exposure in the laboratory;
2. Differences in hydrodynamic flow conditions in the two situations; and
3. Differences in dissolved oxygen and temperature of the seawater in the laboratory compared to the actual hull exposure conditions experienced.

No matter what factor or factors predominate, it is felt that the panel tests are more predictive of actual hull performance than laboratory tests since the hull panels duplicate the actual ship service conditions.

Sheathing Attachment Methods

In the early 1980s, another hull panel experiment was performed to test attachment methods and, again, to evaluate the performance of copper-nickel panels on a ship in service.(6) A group of panels were attached to the hull of the *Arco Texas*, a crude-oil tanker, during construction of this ship at Newport News Shipbuilding, Inc. This ship was designed to be, and in fact is, the largest crude carrier capable of passage through the Panama Canal. Although not initially a part of the exposure plan, the severe abrasion and impact loading attending passage through the Canal provided a realistic, perhaps "worst case" test situation.

Twelve copper-nickel panels, each 0.9 m x 3.0 m and 3 mm thick were divided into four sets of three for emplacement on the hull near the light load line as shown in **Figure** 7. The panels were thus subjected to fully submerged, alternately wet-dry and splash zone conditions. One group was attached by peripheral welding using ENiCu-7 SMAW electrodes reinforced by bonding to the hull with Boskik M-890 epoxy. A second group was attached by peripheral welding with no interior reinforcement. A third group used peripheral welding reinforced with 3M XB-5354 elastomeric adhesive. The last group was attached with the peripheral welds supported by an array of equally-spaced slot welds across the face of each panel.

After two years in service in a wide spectrum of sea service conditions including warm Gulf waters, a number of trips through the Panama Canal, and West Coast waters from Southern California to Alaska, all panels were intact. All panel and welds were tightly adhered to the hull and leak free. There was evidence from magnagage readings that the epoxy and elastomeric adhesives had debonded to some extent during service. These forms of reinforcement, therefore, received no further consideration. Several panels had rather severe scratches and gouges from contact with sides of the Canal, docks or tugs. Thickness measurements before and after service indicated the corrosion loss to be less than 0.025 mm, corresponding to a maximum corrosion rate of less than 0.0127 mm per year. Apparently, the corrosion life of the panels is far in excess of the service life of the vessel.

No evidence of biofouling was apparent on the copper-nickel panels after the two years. The fact that the copper-nickel remained antifouling implies it was also freely corroding during this period, albeit at a very slow rate. Therefore, the panels could not have been provided significant cathodic protection by the surrounding steel hull and they could not have contributed to corrosion of the steel hull, even though the hull paint system immediately around the panels, repaired after installation, had failed to some extent. The hull was host to fouling and after two years had a great deal of algal "grass" several inches-long attached.

Sheathing/Cladding Damage and Galvanic Corrosion of the Hull

The question of rapid and potentially disastrous corrosion of the steel hull plate in the event of damage to the copper-nickel sheathing or cladding has been raised since cladding and sheathing concepts were first introduced. The mean, free corrosion potential of steel is anodic to that of copper-nickel by about 300 mV. Drodten and Pircher at Thyssen Steel AG in Germany carried out tests to evaluate this problem by mounting copper-nickel clad steel test pieces in the immersion zone of a test rig on Helgoland and on the hull of a sea-going tug.(7)

The test pieces were mounted so as to be electrically insulated from the steel test rig or tug boat hull. Holes and slots were machined through the copper-nickel to expose the steel to provide a variety of defect sizes and a range of cathode-to-anode surface area ratios. Defect-free specimens were exposed as well. These were found to be rust-free and free of fouling after exposure. The tug boat was in service at the mouth of the river Ems and, for a period in the cold winter of 1986-87, was used also for ice breaking. The test plates were assessed in a dry dock at intervals of a few months. Individual test pieces were removed for laboratory examination and new ones attached. Some of the test pieces were exposed over the entire test period of 16 months.

Test pieces with larger defects, such as the 5 mm x 100 mm slits, were found after a three month exposure to have profuse rust and fouling. Because of the cathodic polarization of the copper-nickel caused by exposure of the steel at the slit, the fouling resistance of the copper-nickel had, as expected, been lost. Cross-sectioning of the corroded slit defect showed the steel to be undercut by corrosion to about twice the width of the slit in the copper-nickel cladding.

After 4.5 months of service, the test pieces were found not to have the heavy rust and fouling. Again, test pieces were removed and sectioned through the corroded defect in the copper-nickel. Clear differences in the depth of corrosion and in the undercutting, depending on the size of the defect, were found. The 5-mm and 10-mm diameter defects displayed corrosion depth of about 6-7 mm. At the 50-mm diameter defect, on the other hand, the corrosion depth was only 1.5-2 mm.

After a further period of eight months, the tug boat tests were concluded and all test pieces examined in the laboratory. Corrosion depth and undercutting were measured. On the copper-nickel itself, no thickness reduction caused by corrosion, erosion or abrasion was evident after 18 months of ship operation. The original surfaces with the shallow grooves from specimen preparation were practically unchanged.

At Helgoland the test pieces were subjected to one-year of undisturbed exposure in the immersion zone with no interim examinations. Upon removal, light barnacle fouling was found on the surface. The surface at the larger defects exhibited dense marine growth and was covered by dark corrosion products.

The measured corrosion rates and anodic current density values calculated from Faraday's Law are plotted in **Figure** 8 against the area ratios. The influence of area ratio Sc/Sa is unmistakable. The corrosion rate increases up to a limiting value at about Sc/Sa=140. Corrosion rates are higher for the tug boat test pieces in the winter, apparently due to the higher oxygen level of the colder seawater. The water in winter at the mouth of the Ems River contains 11-13 ppm oxygen at about 0 C and only about 5 ppm when water temperatures are 18-20 C in the summer. The corrosion rates are in very nearly the same ratio as the seasonal oxygen level, suggesting that the corrosion reaction is controlled by the rate of the cathodic reduction of oxygen reaction.

The authors conclude that the probability of the occurrence of through-the-hull damage is very small and only likely in the case of a very small defect.

The corresponding situation involving defects in a sheathed hull is somewhat different, as indicated in an experiment on the corrosion of steel in the vicinity of a defect in the sheathing of a steel piling[28]. A small defect in the copper-nickel sheathing will allow a thin layer of water to enter the narrow space between the sheathing and the steel hull bounded by the peripheral sheathing welds to the steel. The Sc/Sa area ratio will be much smaller than the apparent geometric ratio. Corrosion of the steel will proceed rapidly for a very short period until the oxygen is consumed because the entrapped film of water has very poor contact with the outside seawater. It would appear that this situation is less threatening to the integrity of the hull and will allow more than ample time to make a repair to the sheathing.

Hull Roughness

A most important reason for using copper-nickel on the hull of a ship, either by cladding or sheathing, is to achieve fuel economy by virtue of the reduced hull roughness achieved with copper-nickel. The hull roughness is directly related to the shaft horsepower required to overcome simple hull friction; the rest of the power is expended in wave making.

It has been estimated that a shipowner pays a penalty equivalent to a one percent increase in power requirement for an increase of 10 µm in hull roughness (in the range 0-230 µm) and 0.5 percent for every 10 µm beyond that[8,9]. Based on a British study of 400 ships, the average roughness of a new hull is 125 µm, the best attainable roughness is 75 µm, and the average yearly increase in roughness ranges from 50 to 70 µm. A conventional hull, therefore, begins to lose efficiency from the day it is launched, while a copper-nickel hull, if there is any change, contributes to increased efficiency with time.

The roughness data enable calculation of probable ship performance if the entire wetted surface of the *Arco Texas* had been sheathed with copper-nickel. At the end of the test period, the mean roughness of the painted steel hull was 250 µm. The corresponding roughness of the copper-nickel was only 53 µm. The difference, 197 µm, represents the improvement in operational efficiency attainable if the entire hull is sheathed. Assuming the power penalty estimate cited above is valid, full-wetted-surface sheathing with copper-nickel panels would result in a 19.7% improvement in efficiency. An independent study conducted by the Webb Institute supports these findings.[10]

Roughness measurements of the 12 panels of the *Arco Texas* experiment showed that the copper-nickel is considerably smoother at the outset than a painted steel hull, and of considerable interest, the copper-nickel appeared to become slightly smoother after the sea trials. Painted steel, of course, becomes progressively more rough in service. Hull roughness data measured at the end of the *Arco Texas* exposure are shown in **Figure 9.**

Copper-nickel sheet for sheathing, because it is cold rolled, is somewhat smoother than the hot-rolled clad material. Cold-rolled material typically has a mean roughness of about 40 µm, whereas the hot-rolled clad material typically has a mean roughness of about 60-55 µm. Determination of the roughness of the copper-nickel sheathing on the rudder of the *Great Land* showed the roughness to be consistently lower than 20 µm. For comparison, the roughness of the painted steel hull of the ship measured on drydocking after 14 months averaged approximately 210 µm.

SHEATHING METHODS AND COST ANALYSES

State-of-the Art Baseline Method

To effectively analyze the potential operational and maintenance savings for a large ship associated with having a corrosion and fouling resistant copper-nickel hull, it is necessary to have a sound estimate of the cost of sheathing. This analysis was undertaken by the Newport News Shipbuilding Company for the Copper Development Association under a contract from the U.S. Maritime Administration (MARAD).[11]

A ship was first selected for analysis. To suit the purpose of this study, it was determined that a vessel that could be related to both ends of the spectrum of high-block, slow speed ships to low-block, high speed ships would be a desirable choice. For their analysis, Newport News Shipbuilding selected the fleet oiler T-A0 187 class, T-A0 191 series ship as the baseline ship for the study. The block coefficient, wetted surface, and basic ship configuration lend themselves well to comparison with various other vessel types to determine the approximate cost of sheathing of other ships. The dimensions and pertinent characteristics of the fleet oiler are shown in **Figure 10**. The maximum loadline of 38 ft. (11.6 m) above baseline was taken as the line of demarcation for sheathing; i.e., the entire hull below this line would be sheathed including the rudder and sea chests. The sea chests however were not included in the calculations. This gives 83,042 ft² (7,715 m²) of hull to be sheathed.

The sheathing alloy was taken to be copper alloy C70600. The sheet-size selection had to consider the ability to handle and position the sizes commercially available. For the initial analysis, a sheathing sheet size of 48 in x 144 in x 0.1 in (122 cm x 366 cm x 2.5 mm) was chosen. Each sheet would weigh 223 lbs (101 kg). The total welding required was approximately 55,000 linear feet (16,764m). A total of 1,731 full size sheets weighing 424,874 lbs (193 tonnes) would be required. Allowing for cutting to fit around the bow and stem, it was estimated that a total of 2,000 sheets would be necessary.

Based on the weld attachment studies manual SMAW using AWS A5.11 class ENiCu welding electrodes were initially considered. The horizontal plate spacings would be 3/8 in (9.5 mm) and 5/8 in (15.9 mm) on the vertical joints.

An array of 1 in x 3/8 in (25 mm x 9.5 mm) slot welds would be used to strengthen the plate attachment to prevent panting of the sheathing. Section 6 of the American Bureau of Shipping Rules for Building and Classing Vessels was used to determine the hull girder bending stresses. These analyses were conducted at the 1/4-, mid- and 3/4-sections of the hull. The calculated bending moments, combined with section modulus at midship, provided the magnitude of the stresses that act on the vessel about the neutral axis. The frequency of slot welds is dependent on both the calculated stress and the strength of the copper-nickel to steel weld. These calculations indicated that the frequency of slots could be reduced the closer the sheets were to the neutral axis. The results showed that on two-thirds of the hull surface, the slot spacing should be 12 in (305 mm), and on the remaining e-third, the spacing could be increased to 16 in (406 mm). This results in a total of 26,468 slot welds on the ship, and, at least to a first approximation, minimizes the number of slot welds required.

Consulting representatives of various construction departments at Newport News Shipbuilding established the following construction sequence for sheathing:

1. Dock vessel
2. Blast and coat – shot/sand blasting and coating with thin coat of rust preventative.
3. Erect Staging – complete seven-tier staging would be required.
4. Grind Flush Existing Welds – estimated to be 17,000 linear feet (5,182 m).
5. Non-Destructive Test of Existing Welds might be necessary in some cases – cost not included in this estimate.
6. Install Sheathing – mark off, remove coating, tack weld.
7. Weld Sheathing – peripheral and slots.
8. Grind Flush Sheathing Welds – 27,000 linear feet (8,230 m).
9. Remove Staging.
10. Fleet Vessel.
11. Non-destructive Test Sheathing – vacuum test.
12. Undock Vessel.

The time and personnel required for each operation was established. As shown in **Figure 11**, a period of 21 weeks was considered realistic for sheathing. Costs were then estimated for each of the steps above. Information on man-hours to complete a task, length of time in dry dock, unit of time per square foot of area, price for the sheathing material and welding electrode, etc., was required. Results broken down into percentages of total cost are shown in **Figure 12**. In terms of a unit price, the cost was calculated to be \$56.54/ft.^{2} (\$608.59/m^2) (in 1986 dollars). If NDT of the existing steel hull welds is required, this could add \$0.30 /ft.^{2} (\$3.23/m^2) of coverage area.

Improved Sheathing Method

It was recognized that invoking some innovative technology for critical portions of the state-of-the-art approach used above had the potential for substantially lowering the cost. The five major "cost drivers": sheathing material, 25%; install sheathing, 22%; weld sheathing, 15%; staging, 11%; and dry docking, 9%, were analyzed for potential improvements. Three other areas were examined and chosen as secondary areas for improvement; the grinding of existing hull and sheathing welds, and the preparation of the steel hull.

First, the substitution of coiled copper nickel for individual sheets would result in reduced material expense and benefits in lay-off of the hull and placement of material on the vessel. A 24-in-wide coil weighing 7,000 lbs, (3,176 kg) would have a length of over 750 ft (229 m) and could be handled by a special rig to support the coil and allow the material to be unwound against the hull during installation (**Figure 13**). Such a rig should be designed so it could be attached to a typical 15-18 ton hydraulic telescope crane and to the motor-powered, low platform vehicles seen in most shipyards. This equipment would minimize the requirement for the detailed hull layout and facilitate initial placement of the sheathing on the ship. The reduced costs of these items and the material would be partially offset due to the increased linear feet of welding (approximately 20%) because of the smaller width. Semiautomatic welding machines could be used in conjunction with these rigs to tack-weld the sheathing in place. Another significant area of saving, inherent to the use of coil sheathing material, is that this allows most of the expense for staging to be eliminated. Mobile elevated platforms supporting the coils would also allow workers access to any area of the vessel and allow work to progress without lag time for erection of staging.

Ongoing research on welding methods indicated the Metal Inert Gas (MIG) Beam welding technique to be a potentially viable method.[12] The MIG Beam process is a coil-fed, semiautomatic technique requiring only a 1/8-in (3.2-mm) gap which can be filled in a single pass rather than the three passes required for the wider gaps in the SMAW pro-cess. The use of semiautomatic equipment and the single pass reduces the man-hours of labor to complete the task.

Further investigation into the hull girder bending stress of this vessel indicated areas of reduced stresses where the requirements for attaching sheathing to the vessel would be less stringent. As shown in **Figure 14**, approximately 30% of the coverage area required peripheral welds only if 24-in (0.61-m) wide sheathing was used. In the midbody section of the vessel, 36-in (0.91-m) wide material could be used. This region would require a series of slot welds consisting of a 12-in (0.3-m) center-to-center spacing for about 80% of the coverage and 18-in (0.46-m) spacing for the remaining 20%. This configuration reduces the number of slots required from 48,468 to 34,878. The 1-in x 3/8-in (25-mm x 9.5-mm) slots by manual SMAW would again be used.

Another possible area of improvement is to use spot welds. A pulsed MIG spot welding technique developed,[12] has proven effective in all positions. A 3/16-in (4.8-mm) diameter hole with an 82° taper is punched. Three spot welds for each slot weld are required to carry the same load, but the welds could be done semiautomatically. This would eliminate all manual welding on the sheathing and allow for a faster and more effective attachment process requiring a minimum of highly skilled personnel.

Another area where costs can be reduced is in eliminating the grinding of welds. The MIG Beam process does not create large weld beads and would not pose any significant degradation in hull performance. As for the steel hull welds, the copper-nickel sheathing is sufficiently flexible and would essentially conform to the shape of the hull. Only large raised areas need be ground off.

Finally, costs could be saved in hull preparation. The first cost estimate of this study involved sand/shot blasting the entire hull (below the 38-ft. waterline) to white or near-white metal and then applying a thin coating to prevent rust prior to sheathing. Depending on the age of the vessel and the condition of the hull surface at the time of installing the sheathing, only those areas to be welded (butts, seams and slots/spots) need to be cleaned to white metal. Laying off the hull, prior to placement of the copper-nickel sheathing (to indicate the exact locations of the areas to be welded) and then blasting only those areas, would facilitate the process of installation.

Recent developments using the concept of high pressure water as a medium for blasting clean a ship's hull have led to technology that allows specific areas to be cleaned. This system operates by the use of a hand-held, self recovery nozzle that can be limited to a coverage area of only a few inches. Using this or a similar system would allow the areas that are to be welded to be cleaned just prior to the sheathing installation and, therefore, would not require any special treatment to prevent rust.

A revised schedule for sheathing the ship was alculated based on the several improved methods noted above. The total duration for sheathing the vessel is reduced with the improvements to 17 weeks (**Figure 15**). A new cost analysis incorporating these improvements was performed. Costs for the various steps as a percentage of the total cost are shown in **Figure 16**. The final cost estimates based on the improved method was established first for a scenario that incorporates the series of 1-in x 3/8-in (25-mm x 9.5-mm) slot welds welded using the manual SMAW technique.

This leads to a unit sheathing cost of \$35.28/ft² (\$379.61/m²). If the slot welds are replaced by a series of 3/16-in (4.8-mm) diameter spot welds using the semiautomatic pulsed MIG technique, the unit cost is reduced to \$33.18/ft² (\$357.02/m²). A third scenario worth noting is for sheathing during initial construction of the vessel, where certain costs, including drydocking charged to sheathing installation, are eliminated. In this case, the unit cost of sheathing is calculated to be \$25.40/ft² (\$273.30/m²). All of these unit costs are in 1986 dollars and are exclusive of NDT of \$0.30/ft² (\$3.23/m²).

The impact of the improved methods on the individual operations of sheathing is illustrated in **Figure 17**. Large percentage savings result from the reduced requirements for grinding steel hull welds and sheathing attachment welds. The cost of testing the sheathing in this new configuration is the only operation that is more expensive.

Life Cycle Performance Economics

The objective of these studies was to determine the effect of the following three hull-coating systems on the total economics of a sea-going vessel.

- Conventional copper-bearing anti-fouling paint with primer and CP system.
- Organo-tin copolymer antifoulant (OCA) system.
- Copper-nickel sheathing.

Two scenarios for sheathing were considered:

- Having the benefit of sheathing for the full service life of the ship; i.e., sheathing during construction.
- Sheathing as a retrofit after ten years of service.

The analysis presented here used the costs for the sheathing described above to update an earlier economic study performed in 1983.(10) In this study by the Webb Institute, a different ship, a C-4 cargo vessel was considered rather than the T-AO tanker. The C-4 cargo ship is obsolete, but there exists a large body of operating data for it. Analysis of the operation economics for this ship was quite detailed and considered a comparison of a number of factors affecting operating costs and revenues as influenced by the choice of hull protection method.

The cost of sheathing was adjusted for the smaller ship taking into account the reduced installation time due to the smaller wetted area, 46,370 ft² (4,313 m²). The 1983 dollars were inflated to 1986 buying power and the cost of fuel oil was taken as \$18/barrel.

In the analysis of sheathing during new construction, life-cycle economics were based on a comparison of such factors as: engine cost (specific engine-propeller combinations were chosen on the basis of expected coating performance), the cost of the coating methods themselves, fuel consumption, normal drydock costs during the 20-year service life, and salvage revenue. Cargo revenue was held constant for *all* coating systems, a consequence of sizing the engine-propeller combination for each coating method to give the same speed in all cases. The coating's effectiveness is reflected in the size of the engine (a capital cost factor) and the resulting fuel consumption rate.

In the case of the retrofit installation, the life-cycle economic comparison among the three hull protection methods was based on the cost of the coating method, the cost of the extra surface preparation needed to apply the coating at time of retrofit, time out of service, fuel consumption (which would differ for the three methods after installation), drydocking costs during installation, normal drydocking costs during the remaining service years after coating, the cost of coating maintenance, and the added salvage value for copper-nickel at the end of the ship's service life. In retrofitting, the engine size does not change, but fuel consumption would be affected by the coating performance characteristics; i.e., speed. Cargo revenue is, therefore, a function of coating type and is included in the analysis for retrofit coating/sheathing installation.

The results of the discounted cash flow economic analyses are summarized in **Tables 2 and 3**.

In the installation during new construction case, \$1,814,000 is saved as a result of the smaller engine required for the copper-nickel sheathed ship. This partially offsets the substantially higher cost for application of the copper-nickel (even for the lowest cost scenario). But the very large savings in fuel over the 20-year service life results in attractive total savings.

Normal drydock costs arise because the American Bureau of Shipping requires a biannual tailshaft inspection, which requires drydocking. The copper-nickel sheathing

TABLE 2

Economic Comparison of Hull Protection Methods for Installation During Construction.
(All costs in thousands of 1986 dollars.)

Case	Engine Cost	Coating Cost	Fuel Cost	Normal D.D. Cost	Salvage Value	Total Savings
Base (Conv.)	9,200	102	20,263	715	—	—
OCA	8,237	163	17,438	961	—	3,481
Cu-Ni @$56.54	7,359	2,622	14,841	440	19	5,037
Cu-Ni @$35.28	7,359	1,636	14,841	440	19	6,014
Cu-Ni @$25.40	7,359	1,178	14,841	440	19	6,481

should only require a hydroblast, if that, at these drydockings. But, in the interest of being conservative, a small material and application cost equal to two percent of the cost of the sheathing the entire ship was added to allow for the possibility of surface damage. The repair costs for the organo-tin and conventional systems are higher.

Thus the application of copper-nickel hull sheathing at the time of new construction will result in a net savings of from $5,037,000 to $6,481,000, depending on the cost of initial installation. For sheathing as a midlife retrofit after ten years of service, the savings generated by sheathing and the other coating systems are of course not as large.

The "base" case considered here was taken as a complete cleaning of the steel hull to "white metal" followed by application of a conventional corrosion-resistant and antifouling paint system costing $72,000. The sheathing costs are calculated again, using the unit costs described above. Out-of-service time for the retrofit for this vessel is included as a cost at $14,000/day. Drydocking costs have been broken out for those costs associated with the coating process itself and also those normal drydocking costs which the various coating systems will provoke in the last ten years of service. The copper-nickel sheathing will require only half the time in drydock required for either the conventional paint or the OCA coating, resulting in an $83,000 lifetime savings in favor of the copper-nickel. Likewise the labor required to maintain the coatings ("Recoating at D.D.", **Table 3**) will be considered less costly for the copper-nickel sheathing. Fuel savings in this retrofit case accrue only over the last ten years of service and are, therefore, not as large as in the new construction case. But substantial extra cargo revenues *will* result from the smoother hull for the given engine-propeller combination due to higher-speed steaming and fewer days in drydock for maintenance. In the last ten years of operation, the copper-nickel adds $210,000 to the vessel's revenue compared with a conventional coating system.

The net economic result of the copper-nickel application as a retrofit, is listed in the right-most column of **Table 3**. Copper-nickel hull sheathing will save the vessel owner between $343,000 and $1,562.00 compared with conventional paint. An OCA system will result in a $976,000 saving. Reapplying conventional antifouling paint in an "as-new" condition will actually result in a loss of $60,000 since the cost is not fully offset by improved economy and greater cargo throughput. Therefore, even in the case of a tenth-year retrofit, it appears that copper-nickel sheathing can provide higher rates of savings than either conventional or OCA systems, provided that the technological improvements discussed earlier are exploited.

Ship Hull Sheathing – Conclusions

This section has attempted to review the history and experience with copper-nickel ship hulls and to discuss the technology as it pertains to the sheathing of large ships. Experiments with sheathing of the rudder and placement of copper-nickel panels on the hulls of freighters and tankers have provided basis for dismissing concerns over the velocity tolerance of alloy C70600. Galvanic corrosion of the steel hull has been shown to take place at a manageable rate with copper-nickel clad steel with defects exposing the steel. It is suggested that sheathed hulls will be even less susceptible to corrosion of the steel hull in the event of rupture of the sheath. Sheathing employing existing methods as well as easily adopted advanced approaches have been described with the associated costs per unit area. Finally an economic comparison for three methods of hull protection are compared in terms of initial capital cost and savings in maintenance and fuel over the 20-year life of the ship or over a 10-year life in the case of a retrofit sheathing in mid-life of the ship. In both cases, copper-nickel sheathing is shown to result in considerable life cycle cost savings.

We hope this review prompts a study of the potential for copper-nickel sheathing of large ships by world shipbuild-

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* Trademark of the International Nickel Co.

TABLE 3

Economic Comparison of Hull Protection Methods for Installation as Retrofit After Ten Years of Service. (All costs in thousands of 1986 dollars except extra cargo). Cu-Ni total includes $19,000 salvage bonus.

Case	Retrofit Coating Cost	Extra Sfce. Prep.	Time O/O Svc. For Coating	Fuel Cost	Coating Drydock Cost	Norm. D.D. Cost	Recoat at D.D. > 10 Yr.	Extra Cargo Rev.	Total Savings
BASE (Conv.)	72	115	42	20,242	21	165	327	129,020	(60)
OCA	133	115	42	20,212	21	165	510	130,270	976
Cu-Ni @$56.54	2,157	115	1,214	18,394	607	83	220	131,570	343
Cu-Ni $35.28	1,603	115	983	18,445	482	83	220	131,570	1,562

ers and leads to a major demonstration project to advance the copper-nickel ship hull sheathing concept.

SHEATHING OF OFFSHORE STRUCTURES

Introduction

Whereas sheathing of ship hulls for corrosion and biofouling resistance is a concept awaiting a definitive demonstration and test, sheathing of a variety of offshore structures is a proven application for copper-nickel alloys and the nickel-copper alloy Monel* alloy 400. This is because offshore oil and gas drilling and production platforms must maintain their structural integrity and resist the effects of not only aggressive seawater but weather and wave action as well.

With the stabilization of oil prices, the commercial climate for field development has improved. Over 700 offshore fields are reportedly slated for development in the 1990-1995 period. Some 188 of these fields involving 275 platforms are in Asia.(13)

A number of summary papers and reviews of the sheathing of offshore structures have been published.(14-19) This treatment summarizes the salient points with regard to the benefits of sheathing of large offshore structures, *vis-a-vis* reduced structural cost due to elimination of fouling and corrosion allowance due to splash zone corrosion, and gives some insight into the economic benefits.

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 large 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 m below. Lesser amounts of growth extend to lower levels. 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 Seawater

The intensity of corrosion of an unprotected steel structure in seawater varies markedly with position as shown in **Figure 18**. The spray and splash zone above the mean high tide level is the most severely attacked region due to continuous contact with highly aerated seawater and the erosive effect of spray and tidal action. 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 contact with the seawater and, thus, no current flow for much of the time. Corrosion rates are often 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.

Protection of a steel structure can be effected 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. Monel alloy 400 was applied to this task as early as 1949 on an offshore platform in the Gulf of Mexico off the Louisiana coast.(20,21) The LaQue Center at Wrightsville Beach, North Carolina, USA, conducted extensive trials of sheathing using the steel piling supporting the seawater corrosion test wharfs at the laboratory as test specimens. Sheathing or protective materials tested included Monel, AISI 304 stainless steel, 70-30 copper-nickel, and nickel-clad and Monel-clad steel. All of these were reported to be performing very well after 36 years of exposure.(18) 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.(18)

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.

In the early trials, the Monel and the 70-30 copper-nickel alloy sheaths were welded directly to the steel. One might assume that corrosion of the anodic steel below mean low tide would be accelerated because it is in direct contact with the much more noble sheathing material. A number of experiments were conducted at the LaQue Center to investigate this. Kirk has summarized these well.(18) It turns out, that in the tidal zone, steel is by far the most cathodic material, and the more noble sheathing alloys result in lower currents and corrosion of submerged steel than no sheathing at all.

This conclusion is illustrated nicely in the results of galvanic corrosion tests conducted to determine the effects on submerged steel coupled to other alloys in the tidal zone as shown in **Figure 19**. 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. This is because even though the potential difference developed in the noble alloy-to-steel couples is significantly greater than between two steel panels, the more rapid and more nearly complete polarization of the noble metals results in a great reduction in galvanic current. More recently, the International Copper Research Association conducted several research programs clarifying and elaborating on these earlier findings.(22-24) 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.

Fouling Protection

As discussed elsewhere in this series, 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 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 get full advantage of the properties of the alloy. 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(25) or flame-spray. 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 in 1986 ranged from \$18 to \$30/ft^2 (\$194 to \$322/m^2).(17)

TABLE 4

Biofouling Mass on LaQue Test Pilings After Five Years

Piling	kg/m^2	Percent	
Bare Steel	1[illegible]	100.0	
Concrete Insulated	0.36	1.9	Only scattered barnacle shells
Directly Welded	7.95	44.3	
Rubber Insulated	0.26	1.4	Only scattered barnacle shells
Rubber Insulated w/Galvanic Gouple (single point contact)	4.59	25.5	

Biofouling organisms observed - barnacles, oysters, codium,tunicate, colonial tunicate, encrusting and filamentious bryozoans.

Long term sheathed piling exposures to assess the effectiveness of corrosion and biofouling protection and measure the cathodic protection current required for several situations have been sponsored by the International Copper Association and the Copper Development Association Inc. at the LaQue Center for Corrosion Technology, Wrightsville Beach, North Carolina.(26) Over 50 ASTM Type A-36 piling 17-cm in diameter were sheathed with 4.6-mm thick x 3-m long C70600. Some 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. Piling were removed after two year and five-year exposures for study of corrosion of the steel and the fouling.

The results of biofouling accumulation on these pilings are summarized in **Table 4**. The mass accumulated on the bare steel piling was more than twice that on the directly welded C70600 and more than 50 times that attached to the insulated sheathing. Only a few scattered barnacles were seen on the unprotected copper-nickel sheaths after five years.

The galvanic anodes used on the cathodically protected piling were cleaned and weighed; mass loss and consumption rates are given in **Table 5**. In the two-year exposures, the directly welded piling displayed a lower anode consumption rate than the bare steel; the concrete insulated consumption rates was comparable to that of the bare steel. After five years of exposure, both the directly welded and the concrete insulated piling displayed reduced consumption rates. The reduction in anode consumption for the directly welded piling is considered to be due to the

TABLE 5

Galvalum III Anode Consumption and Rates on LaQue Test Pilings After Five Years (Combined Anode Weights*)

Piling Type	Weight Loss (g)	Consumption Rate (kg/yr)
TWO YEAR REMOVALS		
Bare Steel	716.4	0.36
Concrete Insulated	755.3	0.38
Directly Welded	414.1	0.21
FIVE YEAR REMOVALS		
Bare Steel	1880.6	0.38
Concrete Insulated	1256.6	0.25
Directly Welded	687.6	0.14

* Two anodes per piling

favorable polarization characteristics of the C70600 copper-nickel alloy. The reduced anode consumption rate for the concrete insulated piling is most likely due to the high resistance path through the concrete to the underlying steel.

The overall reduction in anode consumption rates for both sheathing techniques could be due to the reduction in current required to maintain a calcareous film formed on the C70600 copper-nickel alloy.

It was also observed that even in the directly welded sheathing technique where piling were 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, no higher than the rate in the freely corroding, unsheathed steel control pilings. Of course, exposure of any steel piling without cathodic protection is not recommended.

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.(27) Biofouling can be quite severe along the Southern California coastline. Bioshield consists of 1-1/2 mm thick 90-10 copper-nickel and a high density elastomer with the trade name 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 loading from the marine growth, was eliminated. The platform was installed in July 1984. After several years, the copper-nickel surface of the Bioshield was free of fouling while the unprotected areas were covered with an 8 - 13 cm thick layer of barnacle and mussel growth. Platform responses were reduced: wave forces, -6%; base shear -10%; overturning moment, -10%; deck deflection, -10%; and pile load, -7%. The reduced platform response values are the reasons that prevention of marine growth can clearly reduce platform costs. Money was saved in reduced steel for corrosion allowance and improved fatigue characteristics in the major platform joints. Estimated savings realized from installing the sheathing system on the 60 conductors from +1.5 m mean low water line to -4.9 m for the 214 m structure were as follows in (1983-84):

Conductors – 55 tons x \$1,000/ton	=	\$ 55,000
Paint – 10,600 ft² x \$3/ft²	=	32,000
Anodes – \$1,250 each x 4	=	5,000
Structural Nodes - 114 tons x \$2,500/ton	=	285,000
Total	=	\$377,000

Estimated savings of \$50,000 to \$100,000 per cleaning was also to be realized. Installed costs for this system on the Eureka platform were reported to be \$250,000 or about \$31.60/ft² (\$340/m²). Clearly, this installation of a copper-nickel sheath system is this example was very cost effective.

Exxon Economic Analysis

The Exxon Production and Research Company carried out a generalized economic evaluation(28) for INCRA by means of a computer aided design study of a conventional steel structure as depicted in **Figure 20**. Only insulated copper-nickel alloy sheathing systems were considered as these gave the full economic benefits resulting from prevention 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 and its installation were not included in the analysis because of their variability with means of attachment.

The results of calculations of gross savings on the costs of materials, fabrication and installation for offshore structures deployed under each of the scenarios considered are summarized in **Figure 21**. In the mild environment, total weight savings ranged from 9 tonnes up to 174 tonnes for the various cases, with cost savings up to a maximum of 5% of the total structure cost. In the moderate environment, weight savings ranged from 80 to 404 tonnes and cost savings from 1.8% to 5.9% of total cost. The corresponding figures for the severe environment were 732 to 2,372 tonnes weight saving and 2.9% to 9.3% cost savings.

There were additional savings from reduced cleaning, maintenance and repair costs, which were not included in the Exxon study.

British Gas Experience, Morecambe Bay, UK

The structures deployed in Phase One of the Morecambe Bay gas 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 is protected by zinc anodes attached directly to the steel. An economic assessment(29) indicated that the 90-10 copper-nickel alloy sheathing was more cost effective than either the Monel 400 alloy sheathing or conventional systems using non-metallic coatings with increased steel thickness previously used on British Gas structures.

The certifying authorities required sacrificial steel (12 mm thickness) in this highly corrosive area when a paint system or neoprene wrap is specified. Sacrificial steel is not required with a copper-nickel (or Monel) 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%. Costs were summarized as follows:

System Costs, Million Pounds Sterling

	Protective Coating/Sheathing			
	Paint	Neoprene	Monel	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(a)	unknown(b)	0.15(c)	0.15(c)
Extra Weight (tonnes)	660	660	180	180

(a) Repainting eight years after installation and every five years thereafter
(b) No long-time experience; no large scale repairs assumed in less than 18 years
(c) Minimum maintenance, confined mainly to accident repair

After over two years in service it appears that the copper-nickel alloy sheathing on the Morecambe Bay structures is free of significant corrosion and, despite the fact that the sheathing was attached directly to the steel, there is less marine fouling than would have been expected if there had been no sheathing.

The application described shows a 90-10 copper-nickel sheathing system to have a net cost savings of from 52 to 77% compared to other systems evaluated.

Summary

Test programs on sheathing of offshore piling have shown the steel underlying the sheathing is virtually completely protected. Biofouling of insulated 90-10 copper-nickel sheathing greatly reduces the potential for structure loading due to increased weight and cross sectional area in turbulent waters. An appreciable decrease in the initial cathodic protection current required by the sheathed piling as compared to the bare steel piling has been observed.

Sheathing of support members and conductors of large offshore platforms has been commercially applied. A number of large installations have performed as expected with documented cost savings compared to the unsheathed design.

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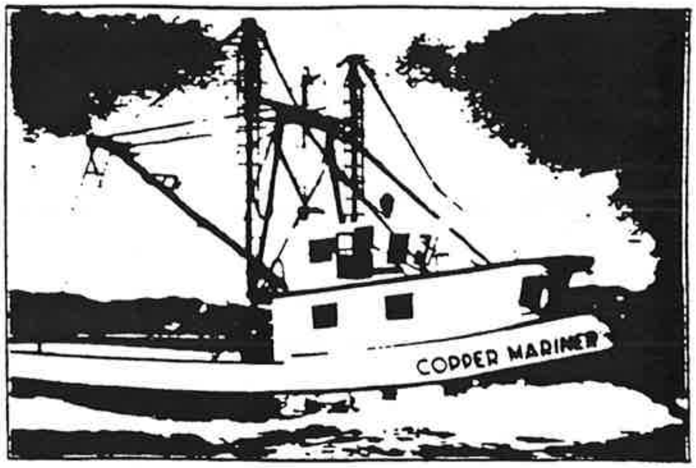


Figure 1 The Shrimp Trawler, *Copper Mariner*

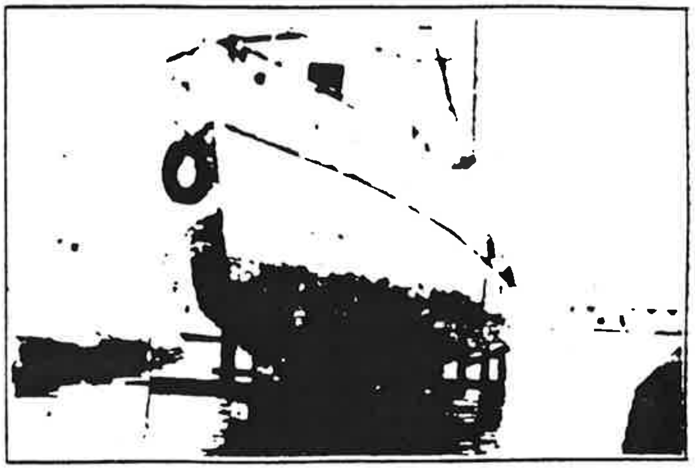


Figure 2 Marine Fouling on the Steel Hull Boat, *Jinotega*, Prior to its Third Cleaning After 18 Months of Total Service.

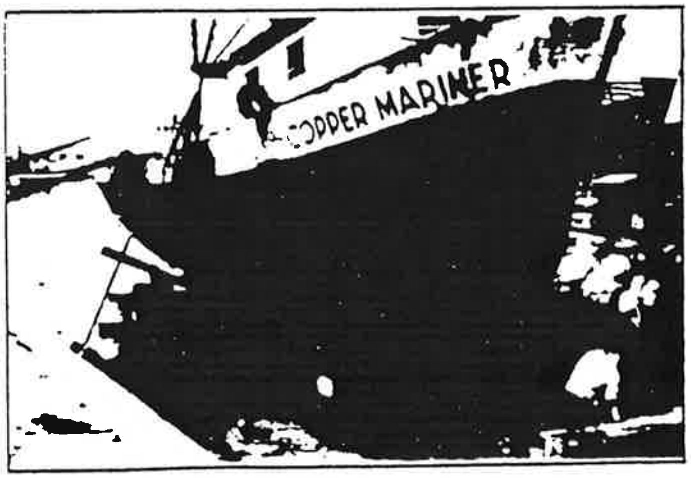


Figure 3 The *Copper Mariner* Hull is Free of Fouling.

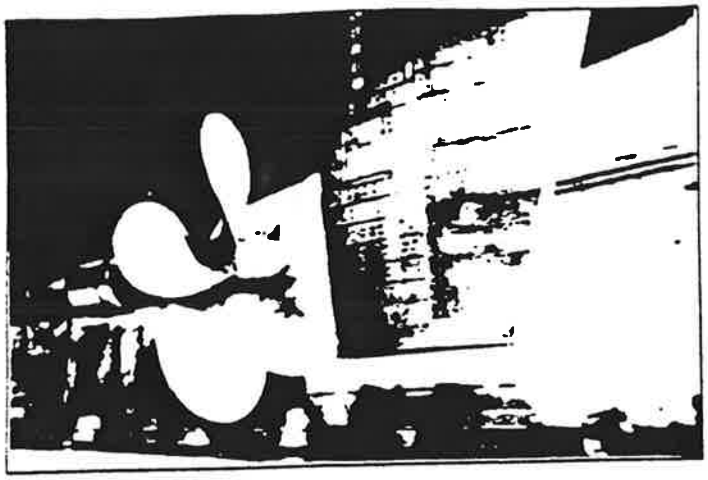


Figure 4 Rudder of the *Great Land* Sheathed in Copper-Nickel.

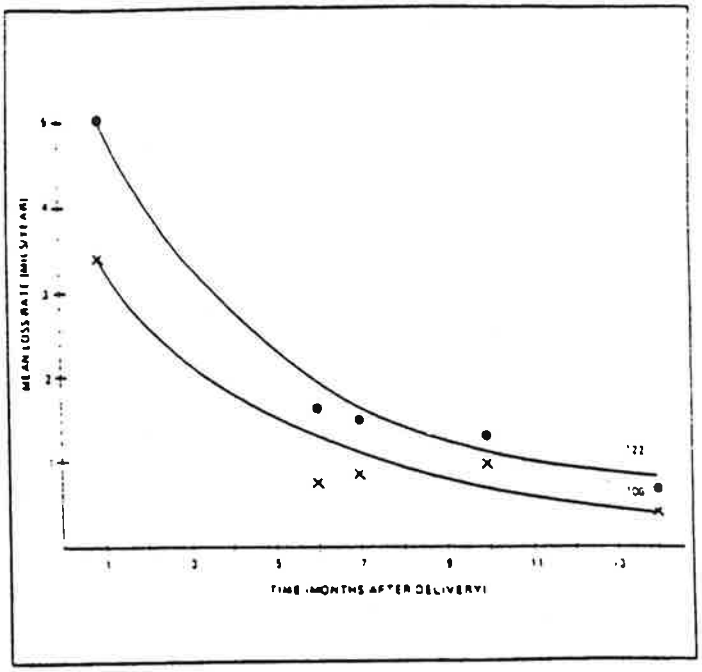


Figure 5 Mean Corrosion Loss Rate vs. Time for the Copper-Nickel Sheath of the *Great Land*.

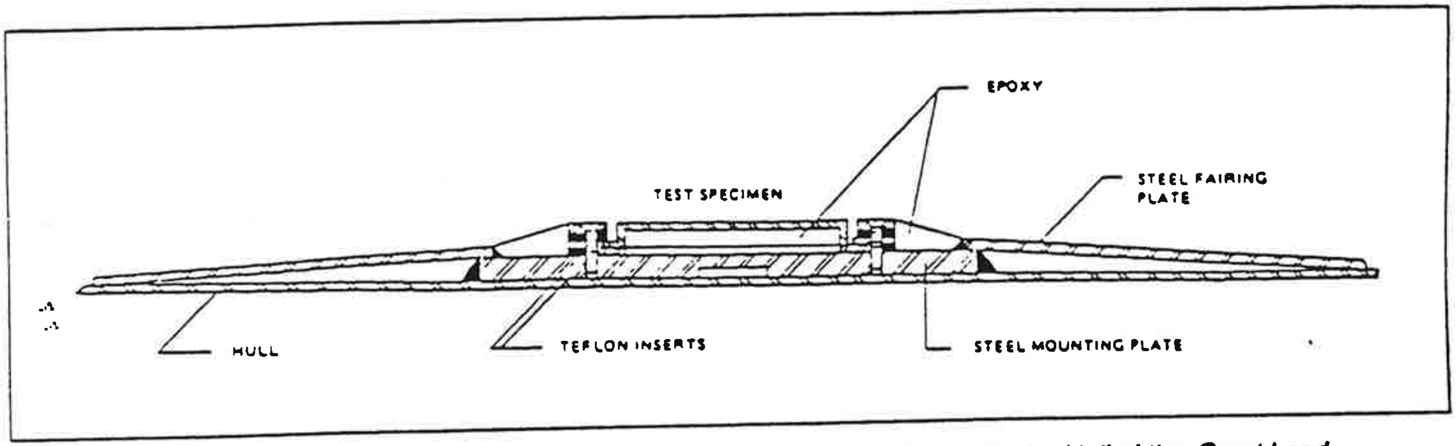


Figure 6 Schematic of Method for Insulating and Attaching Copper-Nickel Panels to the Hull of the *Great Land*.

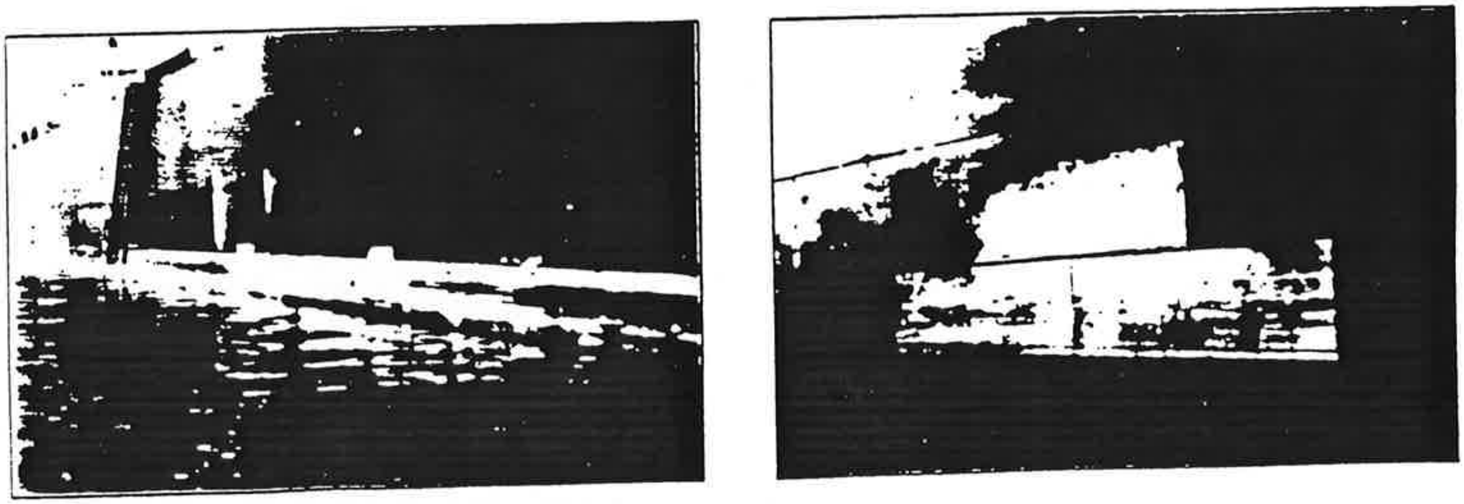


Figure 7 Location of Copper-Nickel Panels on the *Arco Texas*.

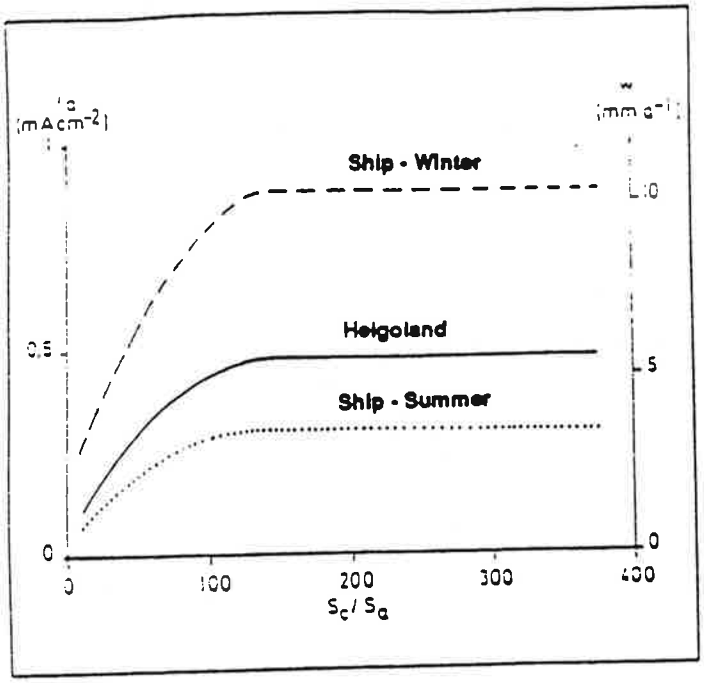


Figure 8 Anodic Current Densities vs. Cathode-to-Anode Surface Area Ratios for Clad Copper-Nickel/ Steel Specimens with Machined Defects to Expose the Steel.

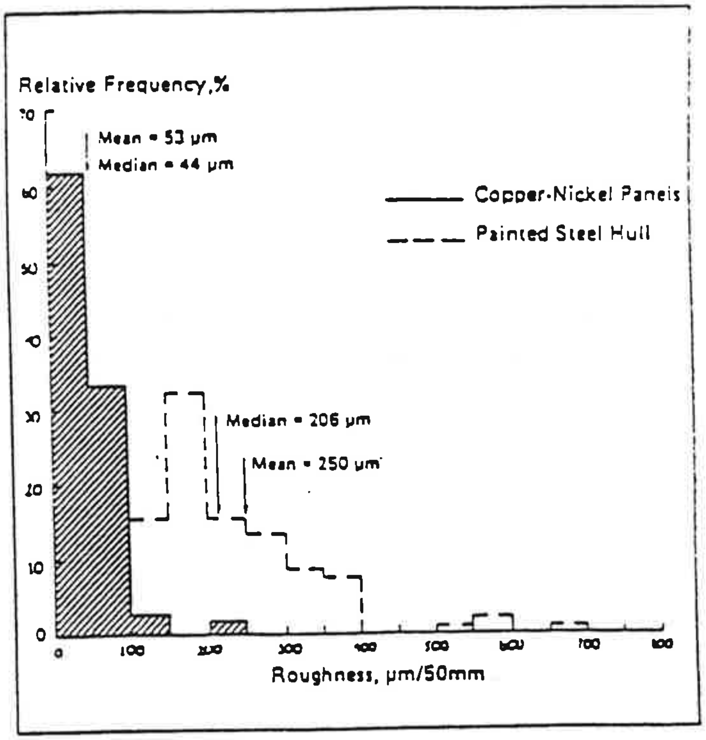


Figure 9 Final Hull Roughness Data at End of In-Service Testing of Copper-Nickel C70600 Panels on the *Arco Texas.*

Length Overall---------------------------677'-6"
Length Between Perpendiculars------------650'-0"
Beam, Maximum----------------------------97'-6"
Draft To Design Waterline-----------------34'-6"
C_b--0.643
Displacement-------------------- 40140 Long Tons

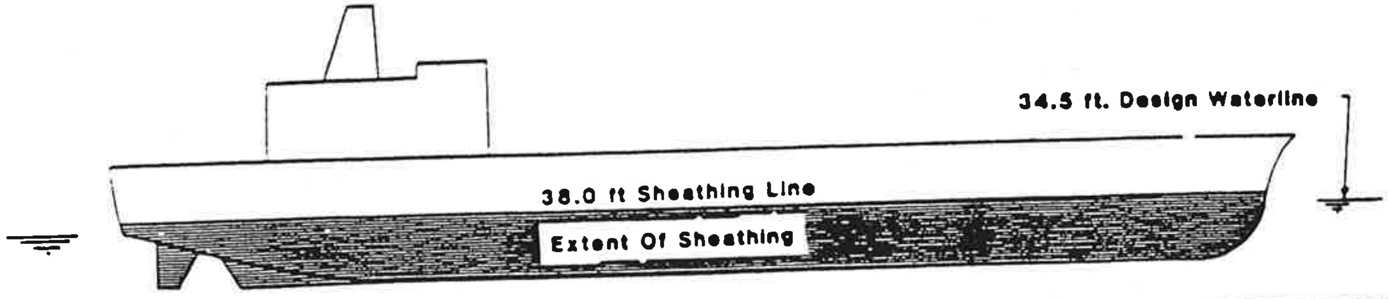


Figure10 Fleet Oiler T-AO 187 Class T-AO 191 Series Profile.

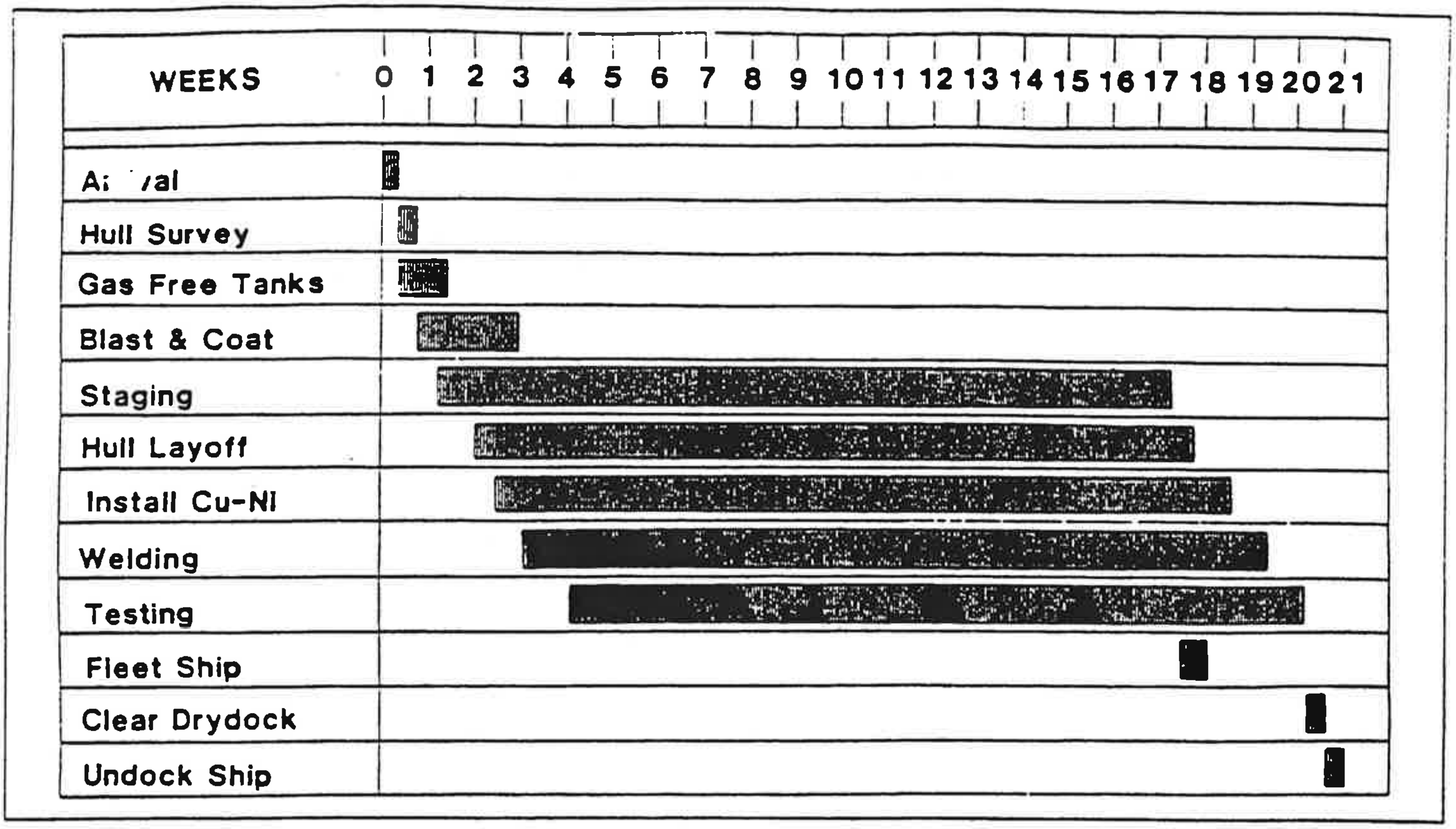


Figure 11 Initial (Baseline) Construction Schedule.

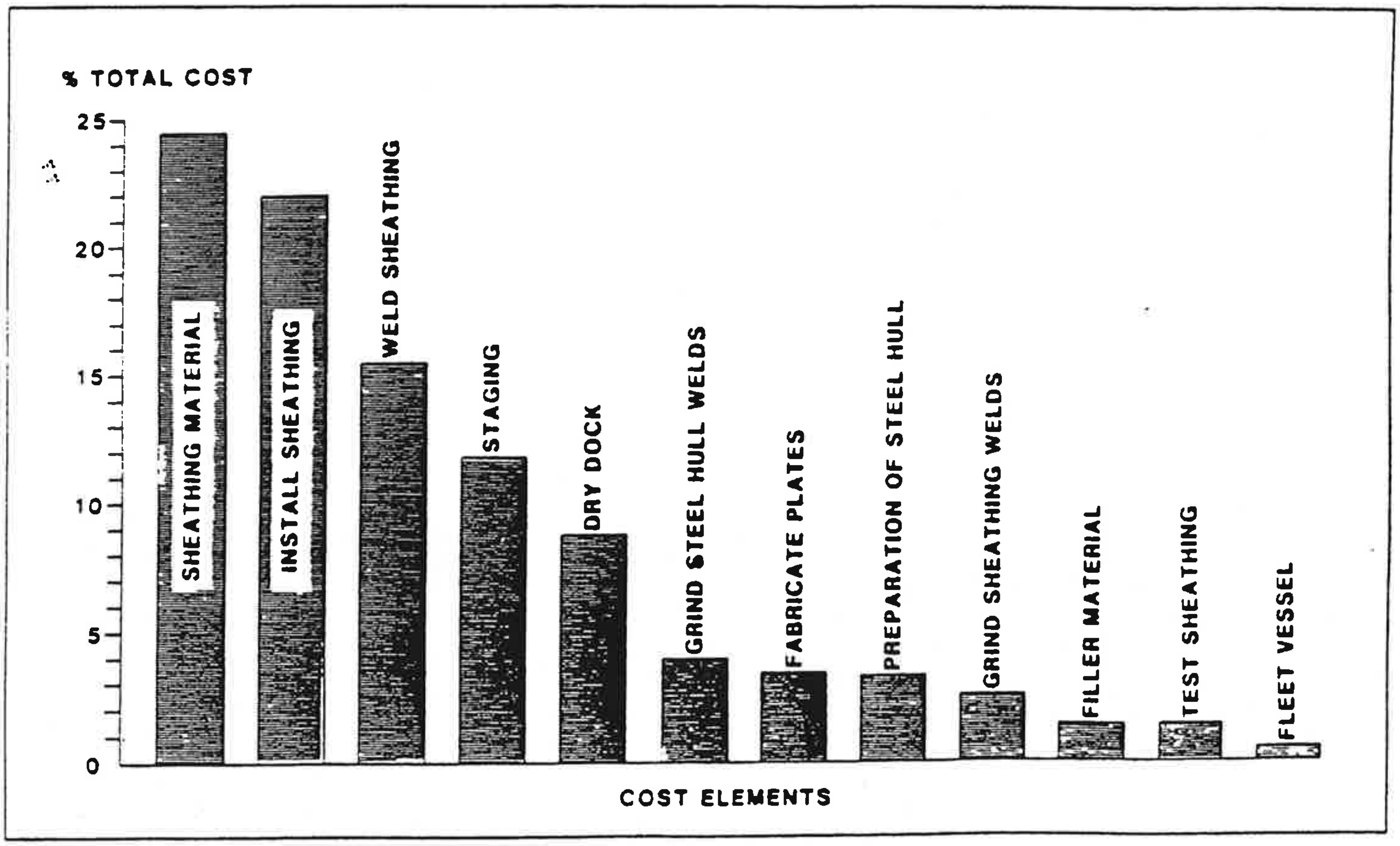


Figure 12 Initial (Baseline) Cost Estimate.

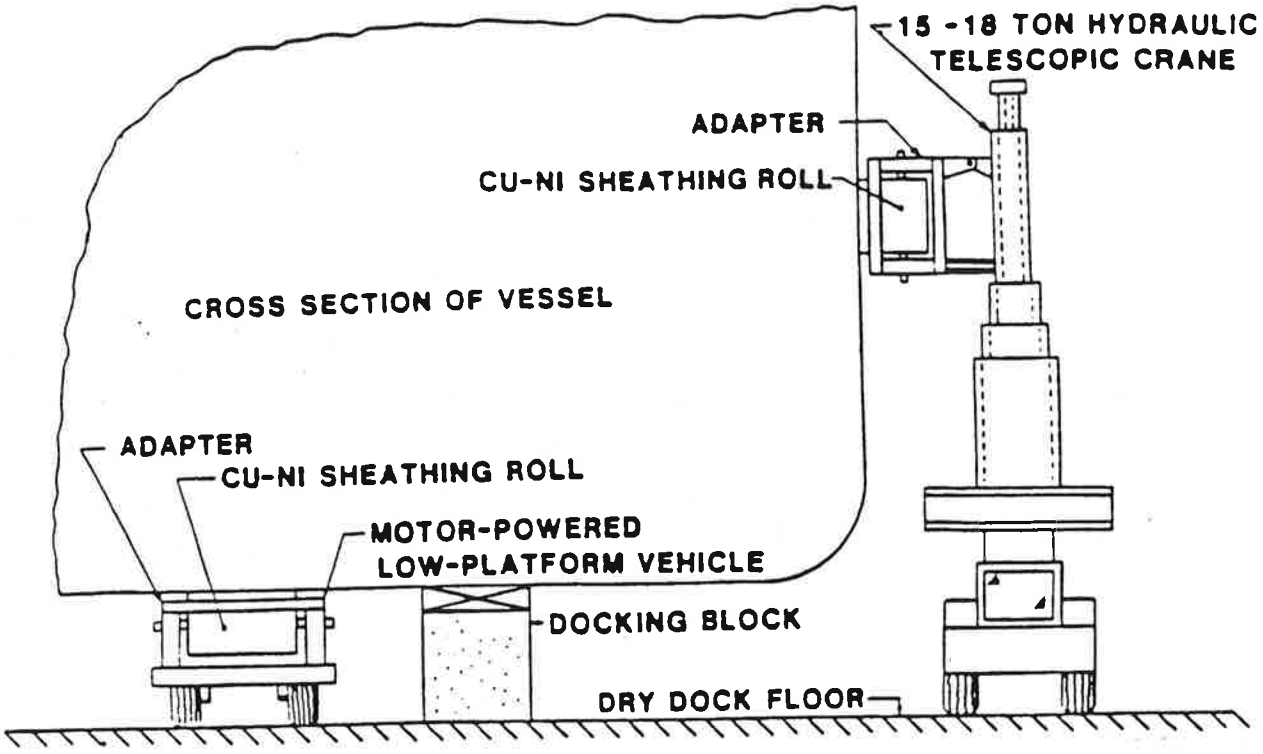


Figure 13 Mobile Work Platform for Coil Handling.

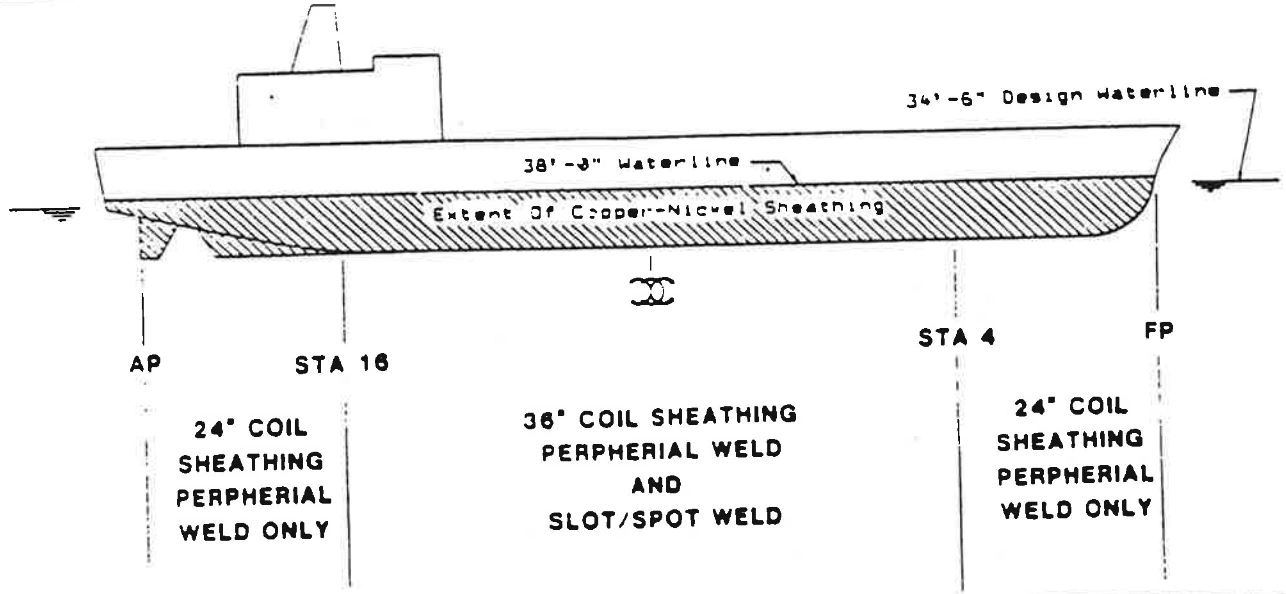


Figure14 Coil Sheathing Arrangement in the Improved Method.

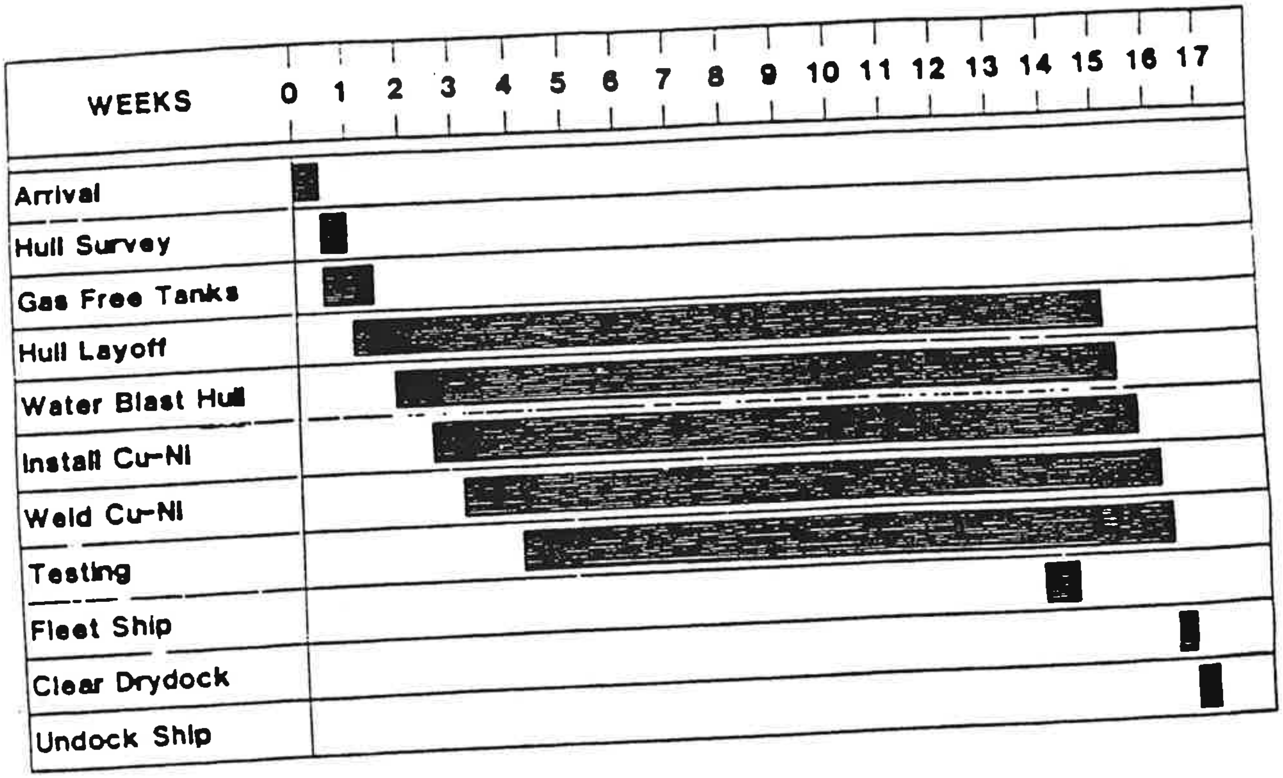
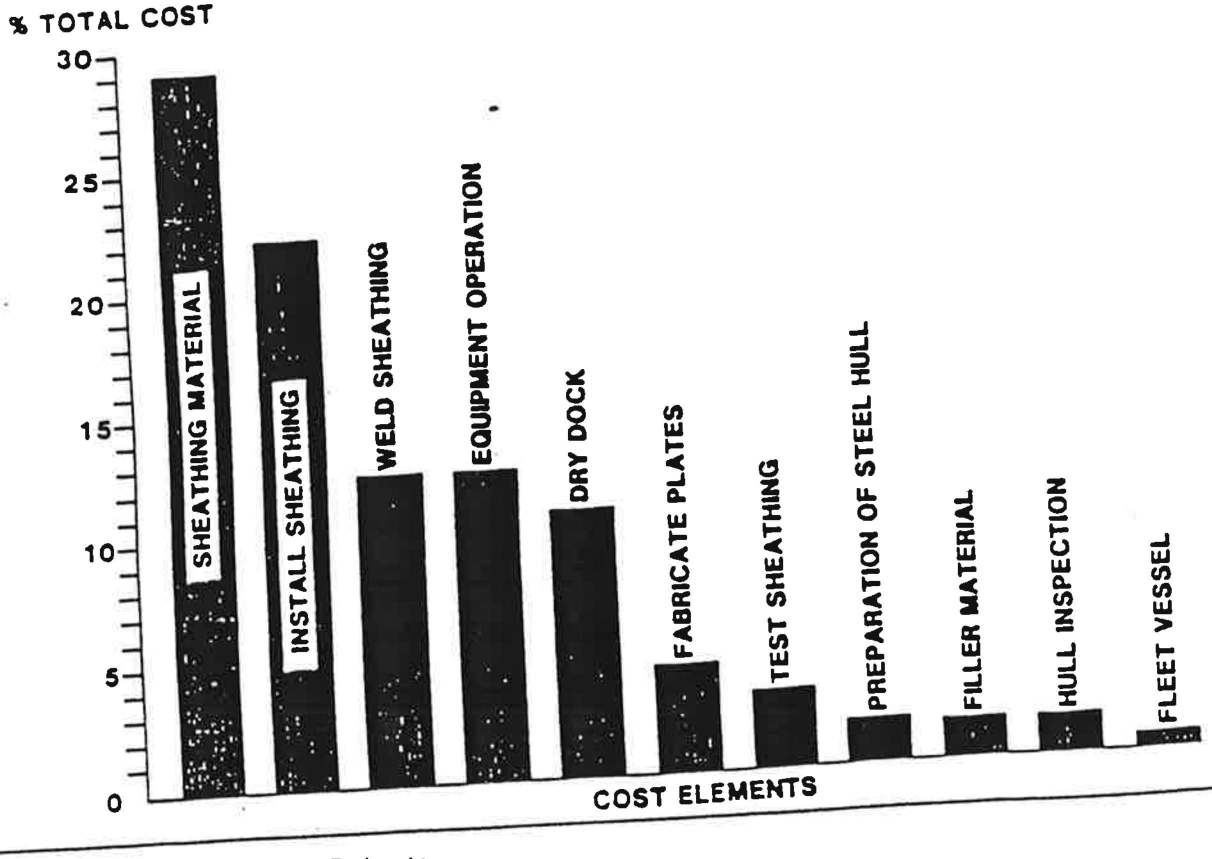
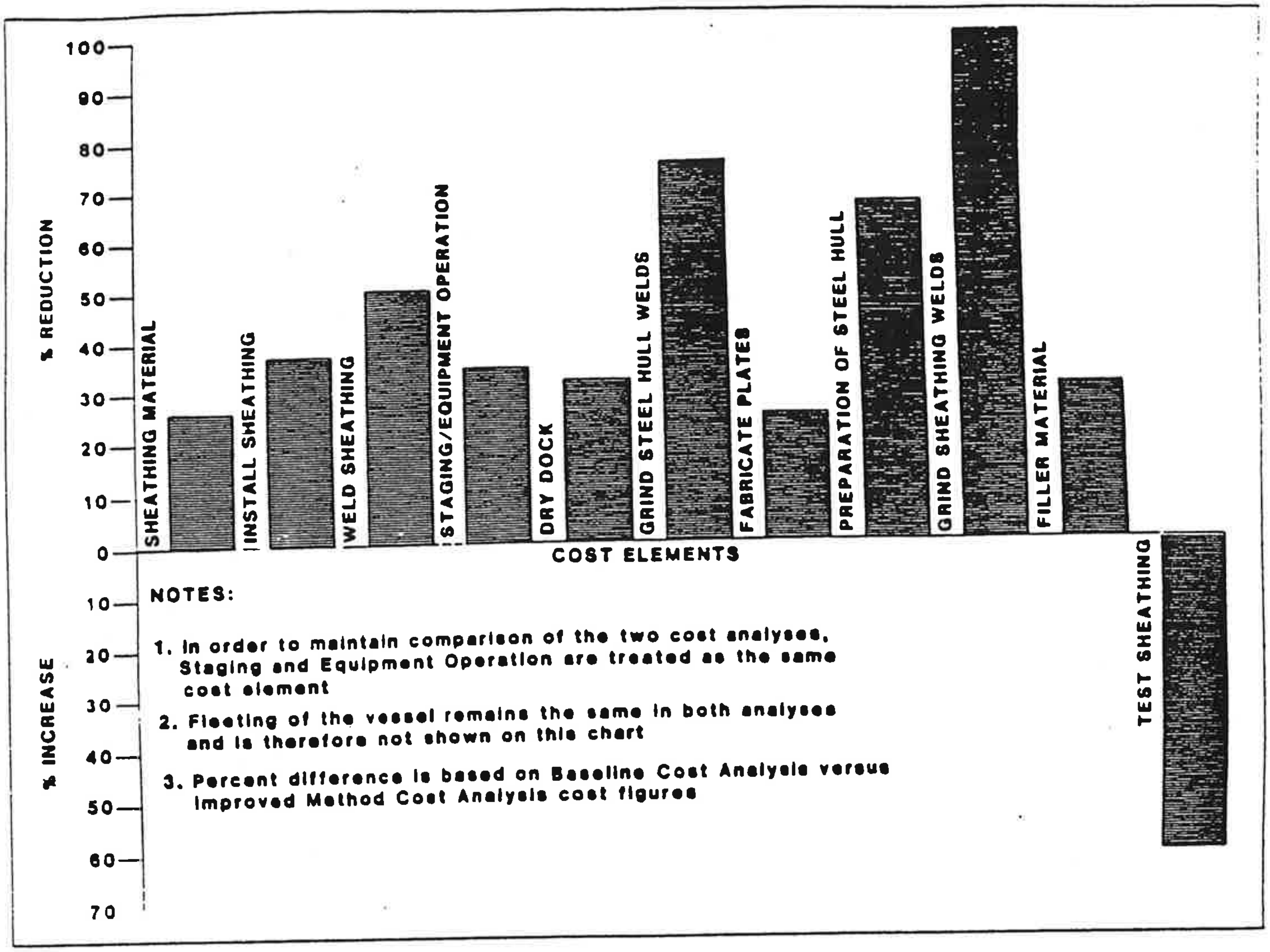


Figure15 Improved Method Construction Schedule.



Method Cost Estimate.



NOTES:

1. In order to maintain comparison of the two cost analyses, Staging and Equipment Operation are treated as the same cost element
2. Fleeting of the vessel remains the same in both analyses and is therefore not shown on this chart
3. Percent difference is based on Baseline Cost Analysis versus Improved Method Cost Analysis cost figures

Figure 17 Effect of Technological Improvements on Cost of the Sheathing Process, Shown as Percent Increase or Decrease for Individual Cost Elements.

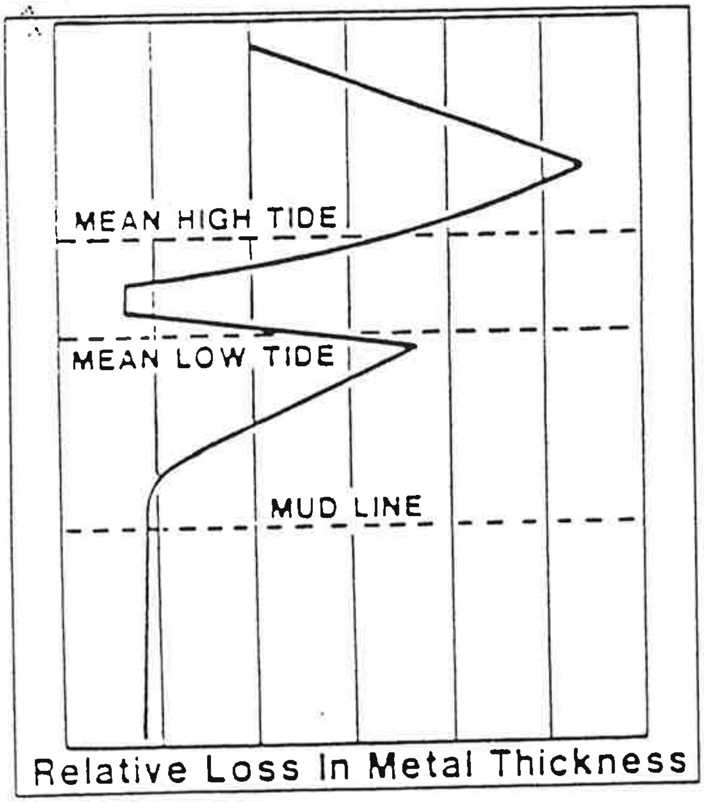


Figure 18 Profile of the Thickness Loss Resulting from Corrosion of an Unprotected Steel Structure in Seawater.

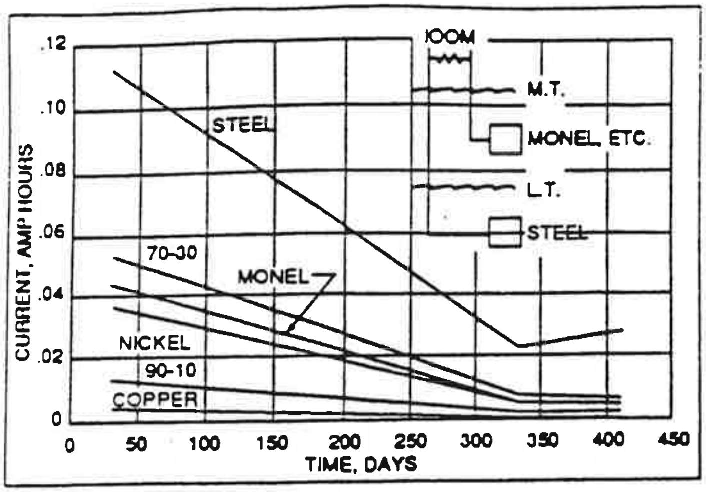


Figure 19 Total Current per Tide vs. Time between Plates in a Simulated Piling Test.

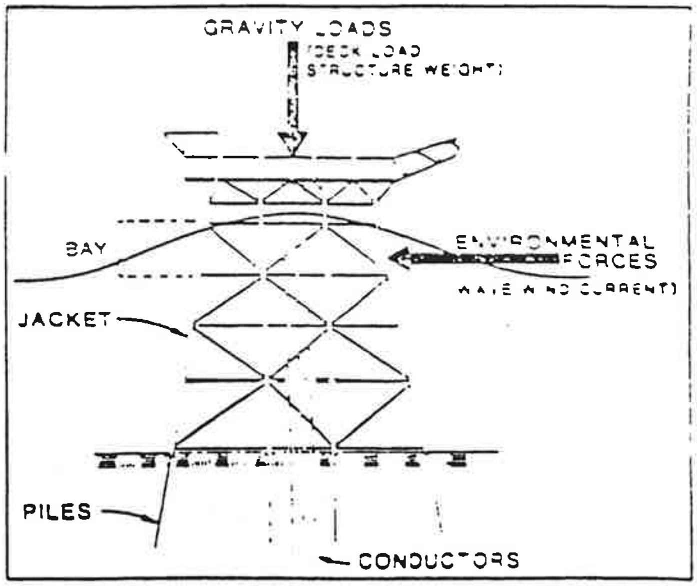


Figure 20 Simplified Diagram of Forces Acting on Off-shore Structures.

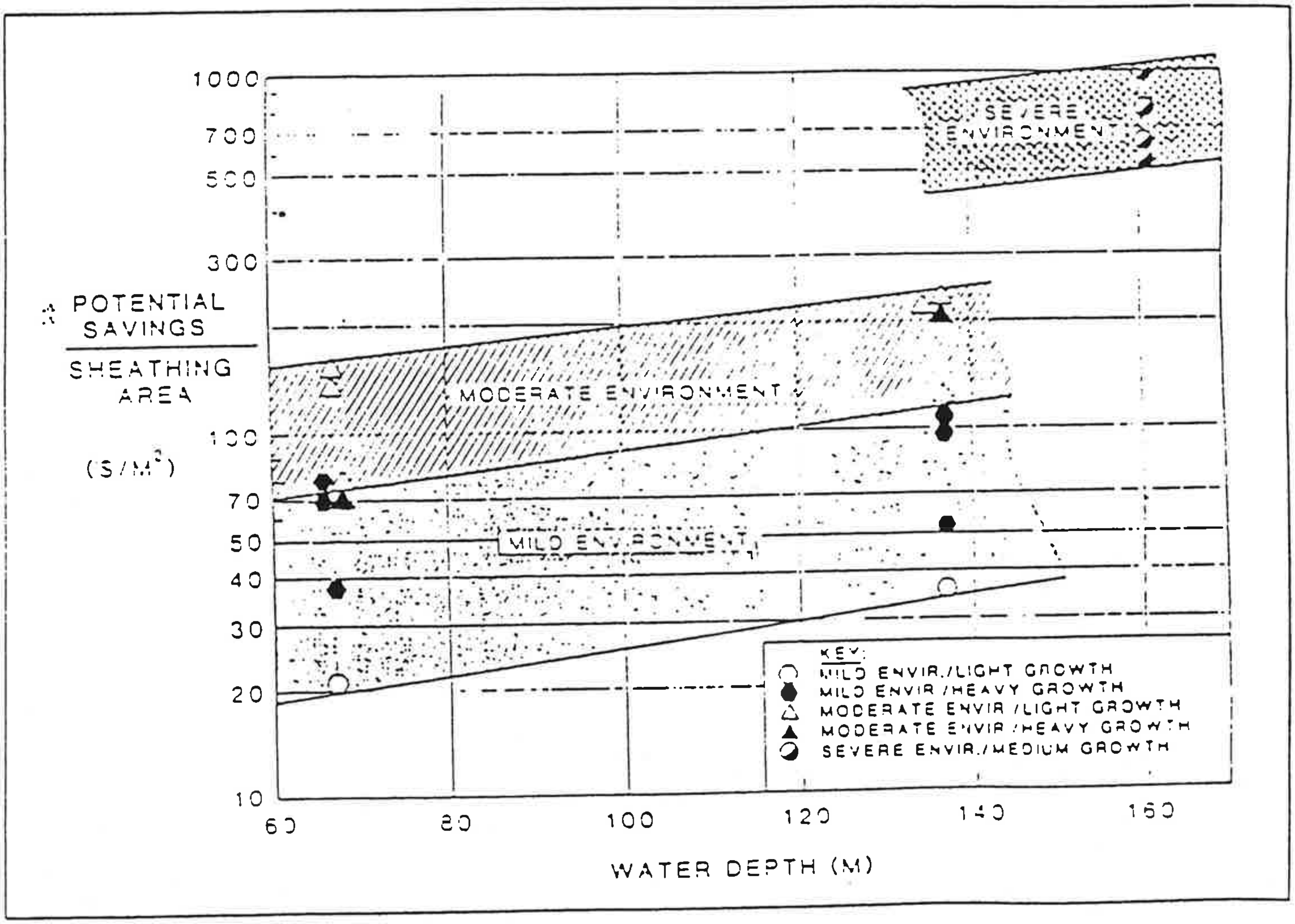


Figure 21 Potential Savings per Unit Area of Sheathing for Various Environments and Water Depths.

JOINING COPPER-NICKEL ALLOYS

RICHARD E. AVERY, Consultant to Nickel Development Institute

Copper-nickel alloys find many applications in marine, power, electrical and chemical industries. Typical hardware fabricated by welding are condenser and heat exchanger components, seawater piping, distillation apparatus and, demonstrating the excellent antifouling qualities of Alloy UNS C70600, the hull of an ocean going commercial fishing vessel, the Copper Mariner. **Figures 2 and 3**, page V - 13, show a comparison of fouling on a copper-nickel hull versus a steel hull. The composition of common copper-nickel alloys and filler metals is shown in **Table 1**.

Most alloys of copper-nickel are solid solutions as shown in **Figure 1**. They may be work-hardened to tensile strengths above the 60 Ksi (410 MPa) level. Typical annealed properties are of 15-20 Ksi (100-140 MPa) yield strength and 40-50 Ksi (275-350 Mpa) tensile strength. Alloy C71900 has alloying additions which enables it to be heat treated to a tensile strength of 80 Ksi (550 MPa) and above. The copper-nickels may be used in the work hardened condition as they are highly resistant to stress corrosion.

While copper and nickel are mutually soluble with each other as shown in **Figure 1**, a number of other elements are not soluble in the copper-nickel alloy and if present may cause cracking in the heat affected zone (HAZ) or weld metal. Lead, sulfur and phosphorus are particularly detrimental and may cause intergranular hot cracking in highly restraint joints.[1] It is essential that the surfaces be clean and free of these contaminating elements before heating to a high temperature such as in annealing or welding.

Common sources of the contaminating elements sulfur and phosphorus are marking crayons, paints, temperature indication markers, cutting fluids, oil and grease. Oil- or grease-base contaminants must be removed by solvent cleaning. Acceptable methods include immersion in, swabbing with or spraying with alkaline, emulsion, solvent or detergent cleaners or a combination of these; by vapor degreasing; by steam, with or without a cleaner; or by high-pressure water jetting.

Table 1. COMPOSITION OF COPPER-NICKELS

		Composition, % maximum unless shown as a range or minimum						
UNS Alloy No.	Previous Trade Names	Cu	Ni	Pb	Fe	Zn	Mn	Other Named Elements
C70400	Copper-Nickel, 5%	Rem.	4.8 - 6.2	.05	1.3 - 1.7	1.0	.3-.8	
C70600	Copper-Nickel, 10%	Rem.	9.0 - 11.0	.05	1.0 - 1.8	1.0	1.0	
C71000	Copper-Nickel, 20%	Rem.	19.0 - 23.0	.05	1.0	1.0	1.0	
C71500	Copper-Nickel, 30%	Rem.	29.0 - 33.0	.05	.4 - .7	1.0	1.0	
C72500	Copper-Nickel, Tin	Rem.	8.5 - 10.5	.05	.6	.5	.2	1.8-2.8 Sn
ERCuNi (a) (C71580)		Rem.	29.0 - 32.0	.02	.4 - .75	(c)	1.0	.25 Si, .02 P, .2 - .5 Ti
ECuNi (b) (W60715)		Rem.	29.0 - 33.0	.02	.4 - .75	(c)	1.0 - 2.5	.5 Si, .02 P .5 Ti

(a) ANSI/AWS 5.7-84 (b) ANSI/AWS A5.6-84 (c) Total of lead, zinc, tin and all other elements not named shall not exceed 0.50%

A typical procedure to remove oil or grease prior to welding includes:

- remove excess contamination by wiping with clean cloth;
- swab the weld area (at least 2 in. (5 cm) each side of the weld) with an organic solvent such as aliphatic petroleums, chlorinated hydrocarbons or blends of the two. Use only clean solvents (uncontaminated with acid, alkali, oil or other foreign material) and clean cloths;
- remove all solvent by wiping with clean, dry cloth;
- check to assure complete cleaning. A residue on the drying cloth can indicate incomplete cleaning.

All the commonly used welding processes are applicable to the copper-nickel alloys. A nominal 70-30 copper-nickel filler metal with titanium as a deoxidizer is almost invariably used to weld all of the copper-nickel alloys. A 90-10 copper-nickel bare filler metal and a covered electrode is available in Europe and occasionally used, but the bare wire is generally limited to gas tungsten arc welding (GTAW) gages up to 0.125-in. (3-mm) thick. Welds made with 90-10 copper-nickel fillers should be limited to non-wetting surfaces since the weld may be anodic to the base metal. Guides for the various welding processes follow.

SHIELDED METAL ARC WELDING

For shielded metal arc welding (SMAW), the flux covered electrode ECuNi is used with direct current electrode positive (reverse polarity). If the arc length is kept short, the weld pool can be controlled in all positions with a 3/32- or 1/8-in. (2.4- or 3.2-mm) diameter electrodes. Long arc lengths should be avoided because of the tendency to cause weld metal porosity. The electrodes should be operated within the manufacturer's recommended current ranges. Excessive amperages will result in weld spatter and undercut at the edge of the weld, especially when the base metal melting point is significantly below that of the filler.

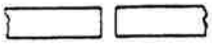
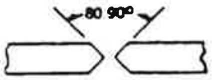
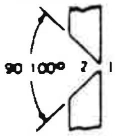
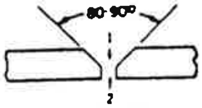
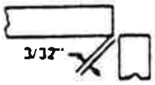
Weld defects are more likely to occur at arc starts and stops. In starting the arc, the proper technique is to strike the arc at some point in the joint so that the metal is remelted. In completing a pass, the arc should not be abruptly extinguished leaving a large weld crater. One acceptable technique is to hold the arc over the weld pool for a few moments and then move quickly back, lifting the arc from the completed weld.

An open root gap and wide groove angle improves penetration and assures good fusion. Tack welds at least every six inches are needed to maintain the opening.

A square-groove preparation for plate up to 1/4 in. (6.4 mm) has been used for flat position welding as shown in **Table 2.** The more common practice is to limit the square-groove to 1/8 in. (3.2 mm) with a root opening at least half the sheet thickness. For out-of-position welding, beveled grooves are required. The procedures presented in **Table 2** were used for joining 1/4-in. hull plates of Alloy C70600 by the SMAW process. The current settings shown may be useful as a guide in establishing parameters for other jobs. The proper setting will also depend on the nature of the duty cycle and power source.

Both stringer and weaving techniques are successful with copper-nickel alloys. However, weaving is usually

Table 2. PROCEDURES FOR JOINING 1/4-INCH THICK HULL PLATES OF ALLOY C70600 BY THE SHIELDED METAL-ARC PROCESS (a)

POSITION	downhand	vertical (b)	horizontal	downhand (1st pass) overhead (2nd pass)	vertical (b)
Edge Preparation (c)					
Gap, in.	1/8	3/32-1/8	1/16-1/8	3/32-1/8	3/32
Number of Passes	2	2	2	2	1 or 2 (d)
Filler Size, in.	1/8	3/32	3/32 (1st pass) 1/8 (2nd pass)	1/8 (1st pass) 3/32 (2nd pass)	3/32
Current, amps	115-120	85-90	100 (1st pass) 100 (2nd pass)	100-115 (1st pass) 95-100 (2nd pass)	85

(a) ECuNi electrode
(b) Welding uphill
(c) Backgouge to a wide V between passes. Tack weld every six inches to hold gap.
(d) Where accessibility permitted, one pass was made on each side.

necessary for vertical uphill and overhead position welding. Weaving should be limited to no more than three times the core wire diameter.

Between passes, surfaces should be cleaned of flux by chipping and/or grinding. When backgouging in preparation for welding from the opposite side, it is essential to gouge to sound metal and to prepare a wide (80° to 90°) V-groove.

GAS METAL ARC WELDING

Copper-nickel alloys are welded with the GMAW process using deoxidized filler metal and direct current reverse polarity. Argon or mixtures of argon and helium at flow rates of 25-50 ft^3/h (0.75-1.5 m^3/h) are usually used. Spray transfer is generally used for 1/4-in. (6.4-mm) thick and heavier sections, but the process is limited to the flat position. For welding sheet and plate from one side, grooved copper or copper-nickel backing bars are preferred.

Representative parameters used in joining copper-nickel alloys by GMAW spray arc are shown in **Table 3**. Currents on the high side of the range are favored for the higher conductivity, lower nickel content alloys. Stringer beads and thin layers to minimize heat input are usually beneficial.

The ERCuNi filler composition provides welds equivalent in strength to C71500 base metal and greater in strength than C70600. ERCuNi contains 0.20% to 0.50% Ti, which serves as a deoxidizer to prevent porosity and oxygen embrittlement.

Short circuit (GMAW-S) is a relatively low heat input process using 0.035- or 0.045-in. (0.8- or 1.2-mm diameter filler metal and is well suited to weld gages under 1/4 in. (6.4 mm). Argon shielding may be used, but argon-helium mixture gives better wetting and better bead contour. The low heat input allows welding in all positions.

Pulsed arc (GMAW-P) incorporates many advantages of both spray arc and short circuit transfer and is well suited for welding C70600 and C71500 alloys. The electrode diameter is usually 0.045 in. (1.2 mm) and an argon-helium mixture shielding gas gives good wetting and arc action. GMAW-P is adaptable to welding in all positions. A more recent advancement in pulsed welding is synergic or variable pulsed welding. With synergic welding, the welder has fewer welding variables to set and there is an improvement in weld quality.

One observation often made when first GMA welding with ERCuNi filler metal is that the wire temper is noticeably lower than that of iron- or nickel-base fillers. Copper-nickel alloys do not work harden to nearly the same degree so the temper is usually lower. To minimize wire feeding difficulties, low friction cable liners should be used.

GAS TUNGSTEN ARC WELDING

The GTAW process is the preferred process for welding thin gage material, 1/16 in. (1.6 mm) and less, but can be a good choice for gages up to about 1/8 in. (3.2 mm). The all-position operability characteristic makes it an excellent process for pipe welding, particularly for small diameter pipe and the root pass of all pipe diameters. After a GTAW root pass in heavier pipe, the weld is often completed by GMAW or SMAW. Automatic GTAW equipment is available for applications such as tube to tube sheet welds, orbital pipe welding and joining sheet gages.

TABLE 3. REPRESENTATIVE GAS METAL-ARC WELDING PROPERTIES

1/16 in. ECuNi filler, direct current, reverse polarity

Thickness, in.	Edge Preparation	Gap, in.	Voltage, volts	Current, amps	Wire Feed, in. per min.	Argon Flow, cfh
1/8	square butt	0	22 - 28	270 - 300	180 - 200	20 - 30
1/4	square butt or single V-60°	1/16 - 1/8	22 - 28	270 - 300	180 - 200	20 - 30
3/8	single V-60°	0	22 - 28	300 - 360	200 - 240	20 - 30
1/2	single or double V-60°, 1/16 in. face	0	22 - 28	350 - 400	220 - 240	20 - 30
3/4	double V-60°, 1/16 - 1/8 in. face	0	24 - 28	350 - 400	220 - 240	30 - 50
1	double U, 1/16 -1/8 in. face	0	26 - 28	350 - 400	220 - 240	30 - 50
>1	double U, 1/16 -1/8 in. face	0	26 - 28	370 - 420	240-260	30 - 50

Copper-nickel welds made without the addition of the deoxidized filler metal very often have excessive porosity that is not apparent on the weld surface. For this reason autogenous GTA welds should be avoided. Other good welding practices to avoid porosity include a short arc, about 0.03 in. (0.8 mm) and ample weld metal shielding to exclude air from the molten weld metal. Argon is the usual shielding gas and preferred for purging the inside of pipes during root pass welding.

Representative parameters for GTAW copper-nickels are shown in **Table 4**. As with the other arc welding processes, the high conductivity, lower nickel alloys require currents on the high end of the range. Where possible, copper or copper-nickel backing bars are favored.

RESISTANCE WELDING

Copper-nickel alloys with 10% or more nickel content have good to excellent spot and seam welding characteristics due to their low thermal and electrical conductivity compared to copper. Precautions must be taken to assure that surfaces to be resistance welded are clean and free from contaminants.

BRAZING

Copper-nickel alloys are most often brazed with silver-base brazing alloys. Fillers of AWS A5.8 Classifications BAg-1a, BAg-1, BAg-2, BAg-18 and BAg-5 are ordinarily used. Alloys BCuP-5 and BCuP-3 are acceptable for use with copper-nickels of 10% or less nickel. The corresponding UNS numbers are shown in **Table 5a**. They should not be used for alloys with high nickel content due to the possibility that embrittling nickel phosphides will be formed. Copper-phosphorus brazing alloys should not be selected for service in sulfurous atmospheres.

Fluxes of the AWS types FB3-A, C, E are satisfactory for most applications. For furnace brazing, inert gases, exogas, endogas or disassociated ammonia are suitable. The dew point should not exceed 20 F (-7 C). For torch brazing, a neutral flame is used. Brazing clearances of 0.001 in. to 0.005 in. (0.03 mm to 0.13 mm) produces maximum joint strength and soundness.

Molten braze alloys may penetrate and crack copper-nickel alloys that are not stress relieved prior to brazing. Also surfaces should be mechanically or chemically cleaned before brazing. Emery paper is usually satisfactory on pipe and tube. Solvents or alkaline cleaners should be used to remove grease and oil. An effective procedure for pickling to remove oxides is as follows: dip in 5% sulfuric acid at 180 F to 200 F (82 C to 93 C) and rinse immediately.

After brazing, any flux residues should be removed by washing with hot water. Oxides may be removed with the same pickling solution used for cleaning prior to brazing.

SOLDERING

Preparation for soldering is the same as for brazing. Copper-nickel alloys have good solderability when an active chloride type flux is used. It may be of the mildly corrosive glutamic acid-hydrochloride type or stronger mixtures of zinc, sodium and ammonium chlorides. Lead-tin and tin-antimony solders are used for copper-nickel alloys. Copper-nickel alloys are classed as somewhat less solderable than brasses.

DISSIMILAR METAL JOINING AND WELD OVERLAYING

Suggested filler metal for joining copper-nickel alloys to some of the commonly combined other alloys is shown in **Table 5**. The listing is not intended to be exclusive in that welding procedures could be developed using filler metals not listed.

The 70-30 copper-nickel welds have a limited tolerance for dilution by iron. Welds with more than about 10% iron tend to have excessive fissures and develop hot cracks. The ENiCu-7 and ERNiCu-7 fillers (65Ni-Cu) have a higher tolerance for iron and are used in joining to carbon steels. However, they are not a good choice in welding to stainless steels because of limited tolerance for dilution by chromium.

TABLE 4. REPRESENTATIVE GAS TUNGSTEN-ARC WELDING PARAMETERS

ERCuNi filler, direct current, straight polarity

Thickness, in.	Electrode Size, in.	Filler Wire, in.	Current, amps	Argon Flow, cfh
1/16	1/8	1/16	100 - 140	15 - 20
1/8	1/8	1/8	140 - 200	15 - 20
1/4	1/8	1/8 - 3/16	180 - 260	20 - 30
3/8	1/8 - 3/16	1/8 - 3/16	260 - 320	20 - 30
1/2	3/16	1/8 - 3/16	320 - 400	20 - 30

Often a very useful step in making copper-nickel dissimilar metal welds is to overlay or butter the other metal with nickel, nickel-copper or any other appropriate filler shown in **Table 5**. In applying copper-nickel overlays on steel, the usual practice is to apply a first layer with ERNi-1 or ERNiCu-7 and then ERCuNi for subsequent layers. Although a high alloy barrier layer is standard, it is possible to apply ERCuNi by GMAW directly on carbon steel with carefully controlled welding procedures designed to achieve relatively low iron dilution on the first layer.

The submerged arc welding (SAW) process is ideally suited for overlaying large surface areas. Commercial submerged arc fluxes are available for all the nickel, nickel-copper and copper-nickel filler metals.(3) In overlaying carbon steel, the first layer is applied using either an ERNi-1 or ERNiCu-7 filler metal followed by subsequent layers of ERCuNi to reach the needed thickness or composition.

Brazing with BAg-1a, BAg-1 and BAg-2 is suitable for joining copper-nickel to any other copper alloy.

CUTTING

Copper-nickel alloys are not amenable to flame cutting, but plasma arc cutting and carbon arc cutting work well. Band saws and shears may be used for cutting, but allowances must be made for the fact that the alloys are relatively soft and ductile. High-speed abrasive wheels work well for beveling edges and trimming material.

WELDING COPPER-NICKEL CLAD STEEL PLATES

The use of copper-nickel clad steel plates offers considerable material savings in many designs and applications. An example is the 76-foot (25-m) fishing trawler, *Copper Mariner II*, with the hull constructed of 5/16-in. (8-mm), 25% C70600 clad. An extensive welding development program was undertaken prior to construction.(4)

For best corrosion performance, the weld face of the alloy side welds should not exceed 10% iron and preferably be below 6% iron. To reach this iron level, at least two weld passes are needed on the alloy side. The alloy side weld filler metals suggested are:

- ENi-1, ERNi-1, ENiCu-7 or ERNiCu-7for the first or barrier pass from the alloy side on to the backing steel; and,
- ECuNi or ERCuNi filler metal for the top or cover pass(es) on the alloy side. ECuNi and ERCuNi are less noble than ENiCu-7 or ERNiCu-7 and are more compatible galvanically with the copper-nickel base metal.

A wide range of weld joint designs and weld pass sequences have been used for clad steel welding. Factors that influence the choice include; total plate thickness, alloy thickness, welding process employed, accessibility to one or both sides, composition constraints of the cover pass to name the more important. Two commonly used weld joints and procedures are shown

TABLE 5a. BRAZING FILLER METAL UNS NUMBERS

AWS A5.3 Classification	BAg-1a	BAg-1	BAg-2	BAg-5	BAg-18	BCuP-3	BCuP-5
UNS Number	P07500	P07450	P07350	P07453	P07600	C55281	C55284

TABLE 5. - FILLER METALS FOR DISSIMILAR METAL WELDS

Welding of Copper-Nickel Alloys

Metal to be joined to Copper-Nickel	SMAW (UNS)	GMAW and GTAW (UNS)	Comments
	ANSW/AWS A5.6	ANSI/AWS 5.7	
Copper	ECuNi (W60715) or ECuAl-A2 (W60614)	ERCuNI (C61800) or ERCuAl-A2 (C61800)	Preheat to 1000 F (540 C)
Phospor bronzes	ECuSn-A (W60518)	ERCuSn-A (C51800)	
All bronzes	ECuAl-A2 (W60614)	ERCuAl-A2 (C71580)	
	ANSI/AWS A5.11	ANSI/AWS A5.14	
Carbon steel	ENiCu-7 (W84190)	ERNiCu-7 (N04060)	Steel side may be overlayed first with ERNi-1 or ERNiCu-7
Austinetic stainless steels	ENi-1 (W82141) or ENiCrFe-2 (W86133)	ERNi-1 (N02161) or ERNiCr-3 (N06082)	Stainless side may be overlayed first with ERNi-1

in **Figures 2** and **3**. Two basic principles that must be observed in welding copper-nickel clad steel plate are:

- never let the carbon steel weld penetrate the alloy cladding or alloy weld. Steel welds with copper pickup are susceptible to hot cracking. And,
- do not weld with ECuNi or ERCuNi on to steel or exceed about 10% iron in the weld. Welds with higher iron content are susceptible to hot cracking.

SHEET LINING

An alternate to the use of solid copper-nickel alloy or clad steel is applying relatively thin sheets to a carbon steel backing. C70600 has been sheet lined to steel for such applications as ship hulls, rudders, condenser water boxes and sections of off-shore platforms. The geometry of the surface to be covered and liner thickness dictates to a large extent the lining method.

Figure 3, page IV-6, shows a carbon steel water box lined with 0.048-in. (1.2-mm) thick C70600 copper-nickel. The liner was first fabricated by GTAW to close tolerances to fit into the carbon steel shell.⁽⁵⁾ The liner was anchored to the steel by a number of arc spot welds made by the GMAW process. Arc spot welding is not new and is used to apply other iron- and nickel-base alloys to carbon steel. Basically a standard GMAW torch is adapted with a "stand-off" attachment that is used to press against the liner and to establish the contact tip distance.⁽⁶⁾ With preset power source and wire feed parameters, the weld is completed in about one second with additional shielding gas flow time to protect the weld.

Other arc spot weld features and controls include:

- The process can be used on sheet thicknesses of 0.024 in. to 0.078 in. (0.6 mm to 2.0 mm), with 0.048 in. (1.2 mm) being preferred.
- Flat position with intimate contact between sheet and steel backing produces the most reproducible results. With a gap up to the sheet thickness between the sheet and the backing, there is some "flash" of weld metal into the gap, but full strength welds are still realized.
- In vertical position welds, there is a tendency for weld undercut and sagging unless the welding current and welding arc time are carefully controlled.
- Using proper welding parameters, welds have less than about 6% iron on the top surface.
- All surfaces should be free of oil, grease, dirt and oxide scale prior to arc spot welding.

When arc spot GMAW is not practical, for example because of welding position or a heavy gage, mid-sheet attachments can be made by plug welding using precut holes. The holes may be circles or slots, *e.g.*, 1/2-in. (12.4-mm) diameter or 1 in. by 3/8 in. (25 mm by 9.5 mm) slots. Round holes in over about 3/32-in. (2.4-mm) thick sheet should have a tapered side to avoid side wall lack of fusion defects. Slot welds are often easier to weld, particularly when the welding is done on vertical surfaces. In many applications it is also necessary to fillet weld the edges of the sheet to the steel backing. The preferred filler metals for the plug and edge welds are ENiCu-7 or ERNiCu-7.

PIPE WELDING

Copper-nickel alloy pipe is widely used in piping systems for shipboard services, coastal installations, desalination plants and offshore oil production. Small diameter pipes, 2.0 in. (50 mm) and under are often socket weld joints. The preferred procedure for larger diameter pipes is a GTAW root pass with the option of GTAW, GMAW or SMAW fill welding. Most consistent quality and higher productivity is obtained when the pipe can be rotated for downhand welding.

The GTAW root pass may be made by manual welding using either the hand-fed filler metal technique or consumable inserts or by using automatic orbital pipe welding. The pipe interior should be purged with argon using the standard practices for other alloys such as stainless steel and nickel alloys. The manual root pass procedures for copper-nickel are basically the same as for other alloy piping, but the welders may notice the weld metal does not flow as well as an austinetic stainless steel. The pipe joint design for manual welding is usually a V-bevel with a nil root face and root opening or a 1/16-in. (1.6-mm) root face and root opening. The filler metal is ERCuNi, and the torch shielding gas is argon.

Automatic welding copper-nickel with orbital pipe welding equipment offers higher production rates and fewer weld defects. On a large firewater system for an offshore platform, orbital welding was able to reduce welding time to one half that of manual welding and cut reject rate from 15% to 5%.⁽⁷⁾ The joint design tolerances must be tightly controlled and are crucial for successful orbital welding. The recommended joint design for most pipe sizes is a J-groove with a 25° bevel, a 3/32-in. (2.4-mm) radius, a 0.050-in. (2-mm) root face with a 0.03- in. (0.8-mm) extension. **Figure 4** shows a weld head mounted on a copper-nickel pipe and joining a straight section of pipe to a "T" section fitting.

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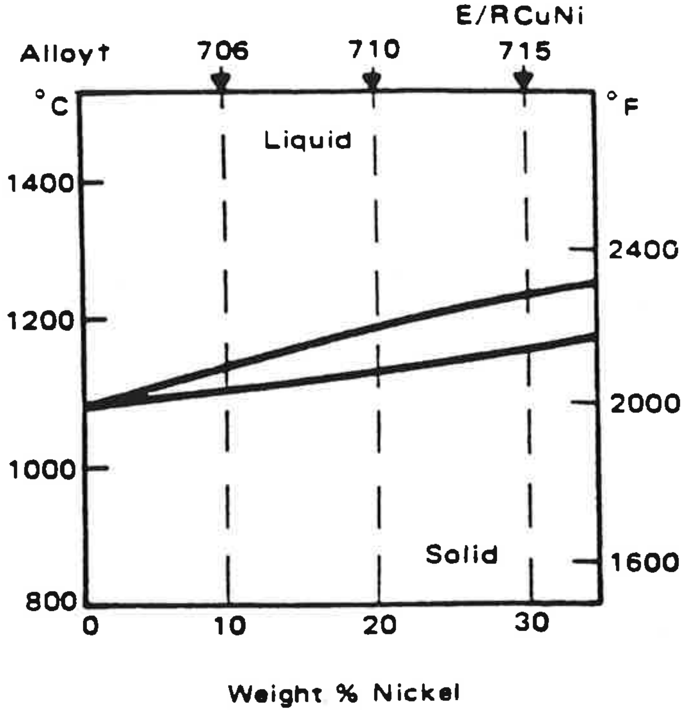
Figure 1 Copper-Nickel Phase Diagram



† See TABLE 1

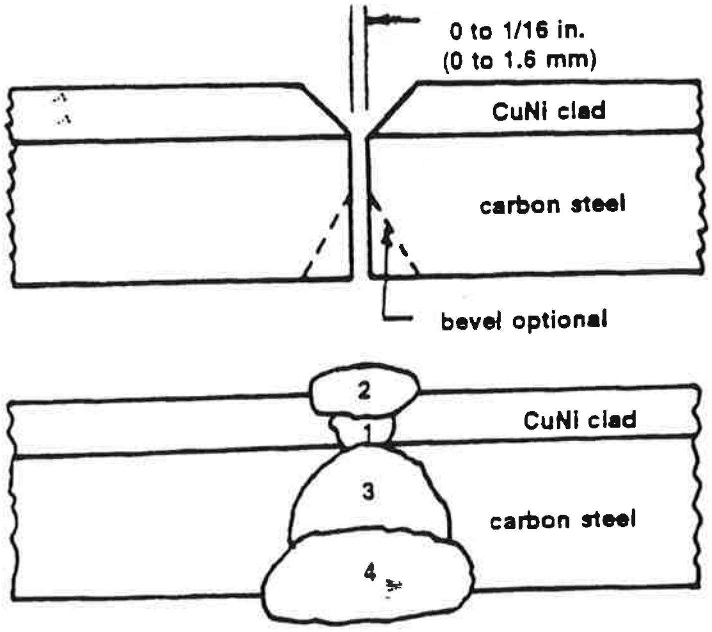


Figure 2 Typical weld joint and bead sequence for copper-nickel clad steel plate 1/2- to 3/8-in. (6.4- to 8.3-mm) thick.

- Pass 1 - use ENi-1, ERNi-1, ENiCu-7 or ERNiCu-7 filler. The top of the weld may require grinding to allow room for pass 2.
- Pass 2 - use ECuNi or ERCuNi.
- Backgouge carbon steel side to clean metal and provide bevel for accessibility.
- Passes 3, 4 or as needed: ENi-1, ERNi-1, ENiCu-7 or ERNiCu-7

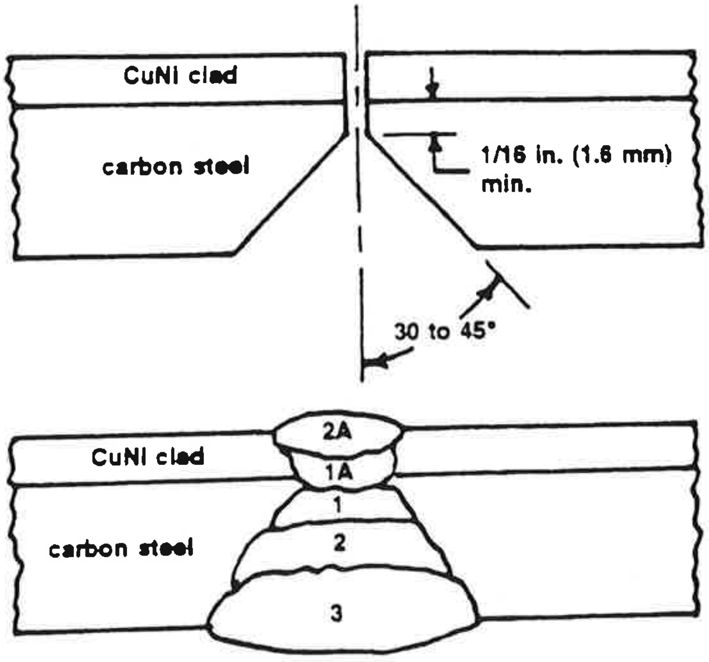


Figure 3 Typical weld joint and bead sequence for copper-nickel clad steel plate 1/2 in. (12.7 mm) and thicker.

- Passes 1, 2, 3 or as needed: carbon steel fillers such as E7018 or comparable filler for GMAW or SAW.
- Backgouge from alloy side to clean metal providing a bevel for accessibility
- Pass 1A - ENi-1, ERNi-1, ENiCu-7 or ERNiCu-7. Grinding top of the weld may be needed to allow room for pass 2A.
- Pass 2A - ECuNi or ERCuNi.

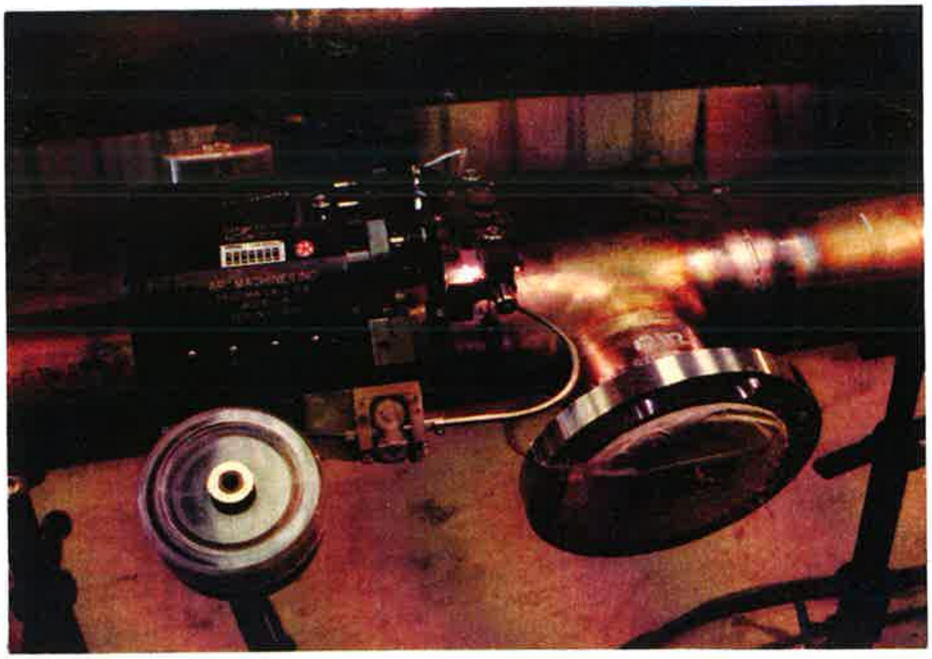


Figure 4 Automatic orbital weld head welding copper-nickel firewater piping. Photo: courtesy Arc Machines, Inc.