Copper-Nickel Alloys for Marine Aquacultural Engineering

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Engineering developments, problems of marine corrosion, fouling and practical innovative applications of copper-nickel alloys in comparison with other materials for marine aquacultural engineering are presented. Coefficient of drag and hydrodynamic force acting on nylon and polyethylene net enclosures have shown a four-fold increase of force in four months at the Cochin Harbour due to fouling. Corrosion behaviour of copper-nickel and other copper base alloys are also presented. Effects of copper additions to culture water are reviewed.

Recent advances in aquaculture presented at the FAO Technical Conference at Kyoto, Japan in 1976 were documented by Pillai & Dill (1979). World production through aquaculture amounts to 6.1 million t. of which India contributes only 0.49 million t. It is estimated that agricultural production through aquaculture will reach about 40 million t. in 2000 AD.

Because of several constraints, marine aquaculture is not widely practised commercially even though it amounts to 0.6 million t (Moreton & Glover, 1980). Even economically viable mariculture practices are beset with several engineering problems, as the vast amount of available engineering knowledge is yet to be pooled for this purpose (Wheaton, 1977). However, during the last decade, attention was focussed on the materials, design and construction needed in aquacultural engineering (Milne, 1972; Anon, 1979, 1981). During the 1970's, extensive works carried out on aquacultural engineering by the Department of Civil Engineering, University of Strathcylde, Glasgow have contributed significantly to commercial aquaculture, particularly in UK, Continental Europe and the Far East (Milne, 1974; 1974 a). The design and development of cages, nets, mesh trays and tanks with corrosion free and fouling resistant cupronickel alloys by International Copper Research Association, USA reflect significant advances in materials technology which made aquaculture a profitable venture. This communication is an attempt to project the prospects of copper-nickel alloys in maricultural practices.

Marine biofouling

Two distinct operations involved before marketing the acquacultural produce are the hatchery and the "grow-out" operations. The former, even for a large scale enterprise is relatively small in physical terms: limited inputs, small quantities of water flow, less space and short period of growth. In comparison to that, the grow-out phase involves large scale man-made or natural facilities for replenishment of water and food for longer period. Nutrient and oxygen-rich, pollution free water needed for mariculture also provides a conducive environment for the luxuriant growth of marine foulers on the netting materials and water conduits used in mariculture. The assemblage of plants and animals constituting the fouling complex poses serious problems and results in increased labour and maintenance. Fouling leads to increased wave action loadings on structures and inhibits the flow of water and nutrients to the animals within the enclosure, thereby inhibiting growth and the productivity of the system.

Copper alloys for ocean engineering

Copper and its alloys have long been recognised as satisfactory materials for several marine applications and are used for diverse purposes in marine aquacultural engineering, offshore gas and oil production, desalination and OTEC systems because of its corrosion and fouling resistance, better heat transfer characteristics, ease of fabrication and long-term economy.

Table 1. *Typical properties and applications of wrought cupronickel*

Alloy type	Forms	Applications
95:5	Wire, sheet, strip and tube	Resistant to marine corrosion notably for sea water trunking
90:10	Wire, bar, sheet, mesh, plate, tube	Components for aggressive waters. Heat exchangers of all types for marine service; for desalination, offshore platform, OTEC system, aquacultural applications such as cages, screens, floats, netting, tank and raceway lining, sheathing of offshore structures and ships hulls
85:15	Sheet and strip	Deep drawn pressings
80:20	Sheet, strip and tube	Heat exchangers
70:30	Wire, sheet, tube, plate, bar	Heat exchanges of all types for marine service; electrical components
55:45	Wire, sheet strip	Electrical resistance and thermo-couples

Copper-nickel alloys with appropriate addition of iron and manganese find wide range of applications in the marine field. The term cupronickel was originally given to an alloy containing copper and nickel in the ratio of 4:1, but the term is now generally used to refer to any copper-nickel alloys containing less than about 50% nickel (Hinde, 1962). The commercial grades used in ocean engineering are those containing copper and nickel in the nominal ratio of 95:5, 90:10, 80:20, 75:25, 70:30, and 55:45. It is the usual practice to denote these alloys by these significant numbers, for example 70:30 cupronickel, though distinct trade names are assigned to each of these alloys.

The composition and typical uses of some cupronickels are summarized in Table 1. The applications are backed by excellent service record for 10 to 20 years all over the world. It is still experimented (Anon, 1975; Huguenin & Ansuini, 1975) under INCRA sponsored marine aquaculture projects for innovative applications. Copper alloy oyster-set-masks are recently employed to control the density, spacing and configuration of the oyster spat. Copper alloy enclosures were also used to protect oysters from oyster drills by providing a barrier which is seldom crossed by oyster drills (Glude, 1966).

Biofouling and drag on netting materials

Large netted enclosures or cages are used in coastal estuaries as in Mariforms, Inc. of Panama City, Florida which maintains a 20 km netting to fence 2,500 acres of penaeid shrimp (Huguenin & Ansuini, 1975). The rapid growth of marine aquaculture industry especially in USA, UK and Japan triggered research on newer materials for netting. Nylon netting is still being used but its progressive decrease in strength and profuse biofouling, limits its use in the tropics. Nylon nets are often damaged by birds, large fish and by floating objects in certain areas resulting in denial of insurance cover.

Milne (1970) studied the seasonal weight increase of several types of netting materials due to fouling under constant immersion in sea water off Scotish coast. Based on this study (Table 2) galvanised welded mesh and galvanised scaffolding were recommended for construction of fish enclosures. These were used initially by the Scotish Marine Biological Association and the Department of Agriculture and Fisheries for Scotland and later by a commercial farm.

Table 2. *Weight increase of netting materials due to biofouling in sea water off Scottish coast (Milne,* 1970*)*

Material	Clean weight N/m^2	July weight N/m^2	September weight N/m^2	November weight N/m^2
Nylon	2.26	6.8	194	240
Ulstron	3.33	10.0	216	370
Courlene	1.96	5.9	169	249
Polyethylene				
a) standard	1.77	5.3	200	350
b) Cupraproofed	1.77	3.5	80	168
Netlon	3.33	6.7	123	163
Plastabond	31.87	35.8	350	446
Galvanised chain link	19.91	25.9	30	74.7
Galvanised weld mesh	33.34	43.3	50	117

Table 3. *Biofouling characteristics of metallic and non-metallic materials in the Cochin Harbour*

Material	Duration of expo-sure, days	Fouling weight, kg m^{-2}	Hydrographic features at test site during exposure (average of 15-20 readings)		
			Surface water temp, °C	Salinity	D.O., ml/l
Copper (plate) (CDA 110)	150	Nil	32.1	31.5	4.4
Naval brass (plate) (CDA 464)	150	0.042	32.1	31.5	4.4
90-10 copper-nickel netting	150	Nil	32.1	31.5	4.4
90–10 copper-nickel-clad steel wire netting	150	Nil	32.1	31.5	4.4
Vulcanised rubber (sheet)	120	3.66	31.3	24.4	5.0
Nylon (rope) (12 mm)	120	3.50	31.3	24.4	5.0
Polyethylene (rope) (12 mm)	120	4.96	31.3	24.4	5.0
PVC insulated armoured electrical cable (10 mm)	120	2.21	31.3	24.4	5.0

During the course of investigations under INCRA sponsored project, Ansuini & Huguenin (1978) reported comparative performance of biofouling resistance of metallic meshes and nylon netting. Exposure to sea water for 18 months has demonstrated the superior antifouling properties of 90/10 copper-nickel mesh with only, 50% blockage to the flow of sea water while it was 95, 75, 75 and 85% in galvanised steel, aluminium bronze mesh, nylon netting treated with copper antifoulant and untreated nylon netting respectively.

Recently while observing the corrosion resistance of certain structural metals in the Cochin Harbour, (Pillai & Ravindran, 1983), the author has studied the biofouling resistance of certain non-metallic materials such as wood, FRP, ferrocement, PVC insulated armoured electric cable, vulcanised rubber, nylon and polyethylene ropes. The results pertaining to the last four materials along with electrolytic tough pitch copper (CDA 110), naval brass (CDA 464), 90/10 copper-nickel mesh and 90/10 copper-nickel clad steel wire netting are given in Table 3.

The fouling organisms that settled on these materials were barnacles and hydroids with fewer algae. However, the barnacles contributed chiefly to the weight of fouling. Oyster settlement was absent in all cases. A detailed account of the fouling organisms that settled and grew on glass panels at the Cochin Harbour is given by Nair (1967). In the case of barnacles growing on twisted nylon rope, the base plate of the animal was found perfectly contoured to the twist of the strands, resulting in a deformation of the normal conical configuration of these animals met with on flat surface. Preferential growth of hydroids was observed on polyethylene rope in comparison to nylon rope. On polyvinyl chloride sheathing also the growth was luxuriant. The barnacles settled on the sheathing were dislodged easily, while the hydroids remained to the base presumably due to the matted growth. The load needed for dislodging a single hydrocoli was found to be 27 g. Thus it is clear that the fouling load on non-toxic materials is considerable even for short periods. The density of foulant on structural metals in the Cochin Harbour (9°58' N 76°16' E) was experimentally found to be 1500 kg m^{-3} and 1450 kg m^{-3} when fouling was dominated by barnacles and oysters respectively. This brings into sharp focus the necessity of suitable designs for supporting and mooring structures to withstand the wave action loading.

Drag on net enclosures

Large flow of water during tidal rise and fall through the net enclosures causes considerable hydrodynamic force on the net, the magnitude of which mainly depends upon the projected area of the body to the plane normal to the current, velocity of current and density of the fluid. The load imposed on the net structures is given by the relation derived by Kawakami (1964) and by assigning proper units to the parameters, the force (N) applied to net can be calculated (Wheaton, 1977).

$F_{c_0} = 4.9\ \rho\ V^2 .\ A.\ C_d$ where C_d, the coefficient of drag is givenby (Milne, 1970):

For knotted net:

$$C_d = 1 + 3.77\left(\frac{d}{a}\right) + 9.37\left(\frac{d}{a}\right)^2$$

For a knotless net:

$$C_d = 1 + 2.73\left(\frac{d}{a}\right) + 3.12\left(\frac{d}{a}\right)^2$$

The coefficient of drag and force for clean and fouled nets can be computed by using these equations. For the latter, the projected area of the net rope under the fouled conditions is to be substituted in the equation.

The coefficient of drag and force for nylon and polyethylene netting materials in the unfouled and fouled conditions after 120 days of immersion in the Cochin Harbour are presented in Table 4. This data permit an evaluation of the drag and force on nylon and polyethylene netting of 2.5 cm nominal mesh size under a water current of 0.8m sec^{-1}. It can be computed that four months of fouling in the Cochin Harbour causes the drag to increase by a factor of about 1.5 and force by a factor of 4, the increase being slightly higher in the

Table 4. *Coefficient of drag and force applied to nylon and polyethylene netting in the unfouled and fouled conditions at the Cochin Harbour* ($\rho = 1022$ kg m^{-3}; V = 0.8 m sec.$^{-1}$; a = 0.025 m)

Material: Nylon or polyethylene (unfouled)

Knotted net			Knotless net		
Dia. cm	C_{d_o}	F_{c_o} N	Dia. cm	C_{d_o}	F_{c_o} N
0.30	1.587	0.763	0.30	1.372	0 660
0.25	1.471	0.589	0.25	1.304	0.523
0.20	1.362	0.436	0.20	1.238	0.397
0.15	1.260	0.303	0.15	1.175	0.282

Material: Nylon (fouled)

Knotted net			Knotless net		
Dia. cm	C_{d_f}	F_{c_f} N	Dia. cm	C_{d_f}	F_{c_f} N
0.608	2.471	2.407	0.608	1.848	1.800
0.544	2.263	1.972	0.544	1.711	1.518
0.476	2.057	1.57	0.476	1.665	1.270
0.403	1.851	1.022	0.403	1.521	0.983
Material: Polyethylene (fouled)					
0.698	2.782	3.110	0.698	2.005	2.242
0.627	2.535	2.547	0.627	1.881	1.890
0.552	2.289	2.024	0.552	1.755	1.552
0.470	2.040	1.536	0.470	1.624	1.223

case of polyethylene netting due to heavy fouling load on that materiial. Fouling prevention and continuous maintenance of fish cages in large scale mariculture need large allocation of funds. The usual practice is to treat the netting with copper based chemicals which by leaching prevent fouling. The antifouling effect generally lasts 1–2 years only necessitating renewal of coats at considerable cost.

Corrosion behaviour of 90-10 *copper-nickel*

The short-term corrosion behaviour and fouling resistance of 90-10 and 70-30 copper nickel panels were determined along with copper (CDA 110) and naval brass (CDA 464) in the Cochin Harbour for 120 days. The panels were subjected to tidal flushing and the water velocity varied from still state to 0.80 m sec $^{-1}$. The results of this test (Table 5) attest the superior corrosion resistance of copper-nickel alloys in sea water.

Table 5. *Results of exposure of metal panels at the Cochin Harbour for* 120 *days*

Material	Corrosion rate micron year^{-1}
90–10 copper-nickel	22.5
70–30 copper-nickel	22.5
Naval brass*	80.0
Copper	61.0

* De-zincification occurred during the test

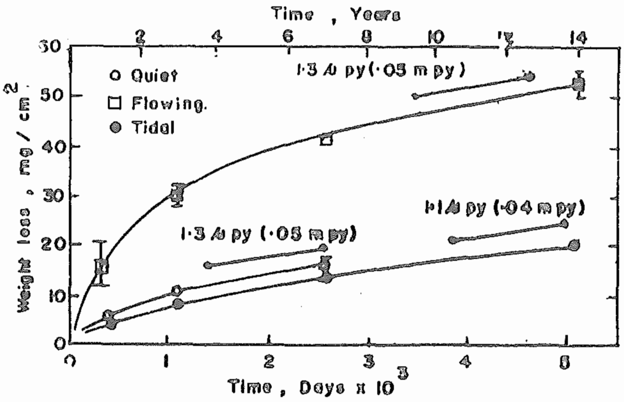

Fig. 1. Chronogravimetric curves for 90/10 copper-nickel in quiet, flowing and tidal zone sea water

The initial corrosion rate of coppernickel declines to very low values with the period of exposure. This can be seen from the equilibrium corrosion rates 1.3, 1.1 and 1.3 micron year–1 for 90/10 copper-nickel in flowing (0.60 m.sec–1), tidal and quite sea water. The progressive corrosion rates, measured by weight loss as a function of exposure period, experimentally determined by Efird & Anderson (1975) are shown graphically in Fig. 1. An increasing number of service records and published works are available on the applications of 90–10 alloy for a variety of marine applications (Efird & Anderson, 1975; LaQue & Tuthill, 1961; Schumacher, 1979).

Copper in marine aqaculture

The resistance of 90–10 copper-nickel to biofouling due to the presence of free copper ions on the metal surface (LaQue & Tuthill, 1961) naturally raises a concern regarding the toxicity of copper ions to fish and shellfish under culture. In fact, this concern deterred the use of copper alloys in fish farms, though copper alloys were widely used in marine applications. It is well documented that though copper is one of the essential trace elements in biological systems, it becomes toxic only when a certain limit is exceeded. In sea and estuarine waters it is reported (Lewis, 1981) that copper may exist in the form of simple aquated ions, metal-inorganic complexes, metal-organic complexes or it may be adsorbed on to/absorbed into organic and inorganic colloidal material (Van den Berg & Kramer, 1979; Lewis, 1981). The available evidence indicates that the free aquated copper ion is toxic, while the complexed form is relatively harmless. The time required for chelation is therefore important as copper is being introduced into the culture water through pumping and storage. An analysis of this aspect led to conclude that the safe limit of copper in culture water would be when it equals copper levels to near coastal and estuarine water which are generally in the range of 2-10 parts per billion (Huguenin & Ansuini, 1975). With this guiding principle, and based on the calculations of the corrosion rates of marine engineering hardware materials such as copper, 90-10 and 70-30 copper-nickel, silicon bronze and phosphor bronze in sea water at velocities of approximately 0.6 m sec –1, Huguenin & Ansuini (1975) constructed a series of curves (Fig. 2) correlating the corrosion rate and computed increase in copper concentration for different values of C which is given by the ratio of the flow of water in gallons per min to the number of square feet of exposed metal. This graph aids to arrive at copper level that is likely to be introduced into the culture water while using different materials. As the background levels of copper in estuarine waters or sea water are generally within 2-10 p.p.b., it

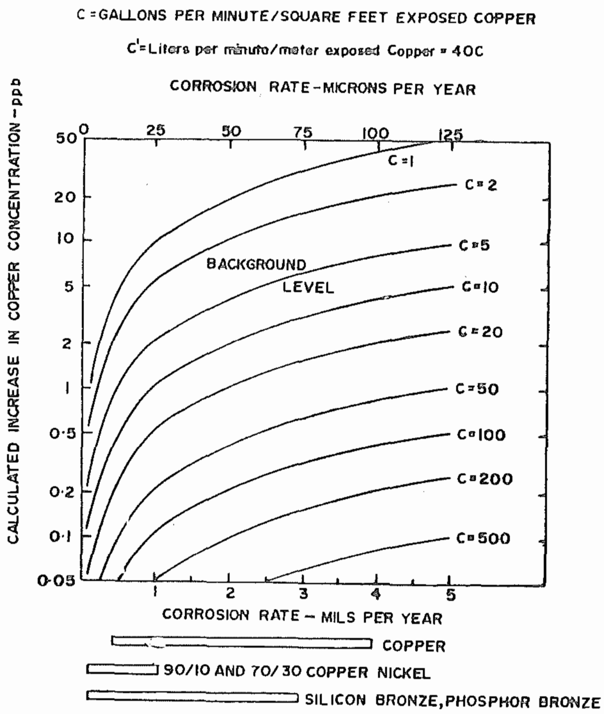

Fig. 2. Increase in copper concentration in culture water at different flow rates for different hardware materials

could be seen from the graph that a value of C=10 can be allowed while using copper-nickels, while for other materials listed a value of C= 20 or greater would prescribe the safe limit. Research under INCRA sponsored projects have shown the technical and economic viability of copper-nickel alloys for large scale marine aquaculture.

Notations used

ρ	–	density of sea water (kg m^{-3})
V	–	velocity of current (m $sec.^{-1}$)
A	–	projected area of net rope (m^2)
C_d	–	coefficient of drag
C_{d_o}	–	coefficient of drag of unfouled net
C_{d_f}	–	coefficient of drag of fouled net
a	–	nominal mesh size (m)
d	–	diameter of net twine (m)
d_f	–	diameter of fouled net twine (m)
N	–	Newton
F_{c_o}	–	Force applied to the unfouled net by current (N)
F_{c_f}	=	Force applied to the fouled net by current (N)
C	–	Gallons per min. ft^{-2} exposed copper
C′	–	40C = Litres per min, m^{-2} of exposed copper

I am thankful to the International Nickel Company Inc., New York for copper-nickel plates, to N. V. Bekaert Societé Anonyme, Belgium for copper-nickel and copper-nickel clad steel wire nettings and to International Copper Research Inc., New York for INCRA Research Reports, to Shri R. Balasubramanyan for his interest in the work and to Dr. C. C. Pandurango Rao, Director, Central Institute of Fisheries Technology, Cochin for his encouragement and permission to publish this paper.

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