Behaviour of Marine Hardware Materials in the Marine Environment

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Seawater, which covers more than 70 % of the earth's surface, is a complex electrolyte containing living matter, suspended silt, dissolved gases and decaying organic materials. Seawater is the most abundant naturally occurring electrolyte. It is also one of the most corrosive natural environment. Despite variations in salinity, temperature and growth of marine organisms from place to place, the general pattern of corrosion of materials remains the same throughout the world. Depending upon the marine zone to which the metals are exposed, the rate of deterioration varies.

A classification of the typical marine environment zone (Schumacher, 1979) is given in Table 1.

Table 1 Classification of typical marine environments

Marine zone	Description	Characteristic corrosion behavior of steel
Atmosphere	Salt laden wind	Sheltered surface may corrode faster than freely exposed areas Corrosion rate decreases with height above water and as one goes inland.
Splash	Wet, well aerated free from fouling	Most aggressive zone for metals. Rust films do not develop protective properties. Corrosion rate exceeds 15 mils per year.
Tidal	Marine fouling likely. Usually water is well aerated	Corrosion is minimum. Oil coating on the surface may also reduce attack.
Shallow water	Seawater usually saturated with oxygen. Pollution, Fouling, sediments etc. may play an active role	Corrosion rate is more than the atmospheric zone. Surface gets fouled heavily
Continental shelf depths	No plant fouling. Animal fouling less with distance from shore. Lower tem. And low oxygen content.	
Deep ocean	Temp. near zero. Oxygen tends to be lower than at surface. Low pH	Often less corrosion. Less tendency for protective mineral scale.
Mud	Presence of sulphate reducing bacteria	Mud is usually corrosive

Mechanical properties

In recent years substantial efforts have been put into the generation of realistic data concerning the selection of materials that are suitable for the most varying requirements in the marine environment. The requirements may vary as in the case of offshore installations where the structure must be strong, reliable and cost effective but in certain critical components, the reliability overweighs the economic considerations. The designer usually locates a material that satisfies the structural requirements first and then seeks to determine how that material will perform in the environment. The basic requirements which merit consideration are the mechanical strength, performance, cost and availability. The elastic moduli and yield strength of several metals, alloys and non – metals (Dexter, 1979) are given in Tables 2 & 3.

Rate factors

Chemical, physical and biological factors influence the amount and rate of corrosion of metals in the sea. The salinity, pH and dissolved gases such as oxygen and carbon dioxide are the major chemical factors while the temperature, velocity and entrapped air bubbles are the physical facotrs of importance.

The major oceans of the world are completely connected in the southern hemisphere and the process of mixing is continuous. The proportions of the major constitutes of natural seawater are uniform, the ratio of water to salt content is the major variant. The total salt content of seawater is expressed as salinity which is defined as the total amount of solid material in grams contained in one kilogram of seawater when all carbonate has been converted to oxide, the bromide and iodide replaced by chlorine and all organic matter is completely oxidised.

Salinity is usually determined by the chemical estimation of the chlorinity (estimation of the chlorides ion content in grams in 1000 g of water) of the seawater and by using the equation;

$$\text{Salinity (parts per thousand)} = 0.03 + 1.805 \times \text{Chlorinity}$$

The salinity of the surface water of the oceans varies typically from 32 to 37.5 ppt. Within this range the corrosion of the metals is not appreciably changed. As large variations in salinity are accompanied by changes in other parameters, the total effect of the system on the corrosion of the metals is to be estimated.

Table 2 Elastic Moduli of ocean engineering materials

Material	Tensile modulus x10^6 psi	Flexural modulus x10^6 psi
Plain carbon steel	30	
HY 80 & HY 100	30	
Low alloy steels	30	
310 stainless steel	30	
Wrought iron	29.5	
Maraging steels	29	
410, 430 & 431 SS	29	
300 SS	28	
Monel 400	26	
Cast iron	23 – 25	
70 – 30 Cupronickel	22	
80 – 20 Cupronickel	20	
Austenitic nickel cast iron	18.5	
Aluminium alloys 7075, 7079 & 7178	10.4	
Aluminium alloys 5083 & 5086	10.3	
Aluminium alloys 5052	10.2	
Aluminium alloys 1100, 3003, 5050, 5456 & 6061	10	
Glass	7.4 – 10	
Epoxy, filament wound composite	6.4 – 7.2	6.9 –7.5
Epoxy reinforced	5.8	5.3 – 5.5
Nylon type 11 & 12	1.7 – 2.1	0.15 –0.17
Polyester sheet molding	1.5 – 2.0	1.0 – 2.2
Polyester glass filled	1.6 – 2.0	1.5 – 2.5
Nylon type 6/6 glass filled	1.4 –2.0	1.0 – 1.8
Graphite	0.5 – 1.8	
Polyethylene HD	0.06 – 1.0	
Epoxies, rigid	0.4 – 0.9	0.45
PVC	0.35 – 0.6	0.3 – 0.6
Nylon type 6 & 6/6, dry	0.38 – 0.54	0.15 – 0.5
Polystyrene	0.4 – 0.5	0.15 – 0.5
Acrylics	0.27 – 0.5	0.3 – 0.5
ABS polymers	0.2 – 0.4	0.2 – 0.4
Epoxies, flexible	0.001 – 0.35	0.36 – 0.4
Polypropylene	0.1 – 0.2	0.1 – 0.25
Nylon type 6/6 & 6/10, wet	0.07 – 0.16	
Teflons TFE & TEP	0.04 – 0.07	0.06 – 0.08
Polyethylene, low & medium density	0.02- 0.05	0.01 – 0.10

Table 3 Yield Strength of Ocean Engineering Materials

Material	**Yield Strength** (a) **1000 psi**	
	High	**Low**
Maraging 300 steel	340 (b)	110
4130 to 4150 alloy steels	250	90
Filament wound epoxy	240 (c)	230
Cast Iron grey	200	50
Monel K 500	195	40
Hy 180 steel	NA	180
431 SS	155	95
410 SS	145	35
Monel 400	130	25
Phosphor bronze CDA 524	116	26
Hy 100 steel	115 (b)	100
Hy80 steel	100	80
70 / 30 Cu – Ni	79	18
7128 Al	78	15 (d)
80 / 20 Cu – Ni	75	17
7075 Al	73	15 (d)
Inhibited admiralty CDA 443	72	13
Silicon Bronze CDA 655	70	21
Naval brass CDA 464	66	25
Manganese bronze CDA 675	60	30
Low alloy steels	60	40
6061 Al	57	8
90/10 Cu – Ni	57	16
Al bronze D CDA614	55	30
7039 Al	50	
310 SS	45(e)	40
304 SS	42(e)	35
316 SS & 316 L SS	42(e)	30
304L SS	35(e)	28
Nylon type 6/6 glass filled	30(c)	20
5050Aluminium	29	8
Wrought iron	27	27
Zinc	27	19
3003 Aluminium	27	6
Polycarbonate glass filled	25(c)	12
Nylon type 6 glass filled	23 (c)	21
1100 Aluminium	22	5
Polyester sheet molding	20 (c)	8
Epoxy rigid	15 (c)	5
Polystyrene	15 (c)	5
Nylon type 6/6	12.6	5.2
Nylon type 6	12.5	7.5
Acrylics cast	12.5	6
Acrylics	10.5 (c)	5.5
Epoxies flexible	10 (c)	1.4
Polycarbonate	9.6	8.0

PVC rigid	9.0	5.5
ABS polymers	8.0 (c)	4.5
Teflons TFE & FET	6.5 (c)	2.0
Polyethylene HD	5.5	2.9
Polypropylene	5.5 (c)	2.8
Neoprene rubber	4.0 (c)	3.0
Graphite	1.7 (c)	0.4

a Where true yield point exists and for brittle materials, the ultimate strength is given.
b Value given is for compressive loading. Tensile yield is about 15 % lower
c Value given is ultimate strength (see note a)
d Seldom used in low strength annealed temper
To convert stress from ibf / sq. inch to Mega Pascal (Mpa) multiply by 6.894757 E – 03

The pH of the seawater varies slightly from 8.0 to 8.2 depending upon the photosynthetic activity and this variation does not exert a measurable effect on corrosion.

Dissolved oxygen in seawater appreciably affects the corrosion of metals. The oxygen level may reach a value of 12 ppm in seawater of salinity 36.11 ppt, the dissolved oxygen attains a level of 5.37 ppm at 30° C. For the common materials an increase in oxygen level favors a higher corrosion rate.

Seawater is a good conductor of electricity. For practical purposes the resistance of natural seawater may be taken as one ohm per foot cubed. The specific conductance of seawater at a chlorinity of 19 ppt at 25° C is 0.052127 reciprocal ohm-centimetre.

The effect of temperature on the corrosion of metal is difficult to predict as the solubility of oxygen decreases with temperature while the biological activity increases. The calcareous scale formation is more likely with increase of temperature.

Flow (velocity) of seawater affects the corrosion of metals and this aspect is to be studied by all designers. Erosion – corrosion caused by high velocity silt bearing seawater, impingement attack where air bubbles are present and cavitation where collapsing vapour conditions of flow. For metals such as copper and iron the corrosion becomes excessive when the critical velocity is exceeded. In the case of passive metals for e.g., titanium, stainless steels and certain types of Ni-Cr-Mo alloys flowing seawater imparts resistance.

Fouling is an important biological factor influencing the corrosion and performance of structures exposed to seawater. Upon exposure of a metallic or non-metallic object in seawater a biological slime film tends to develop on the surface. This film of living bacteria and other microorganisms favours the settlement of embryonic fouling organisms. Corrosion and biofilm formation are simultaneous process occurring immediately upon exposure of the object to seawater. The sessile organisms of the fouling community are of major concern from the corrosion point of view. Fouling organisms such as annelids, barnacles, encrusting bryozoans, molluscs, etc., build hard shells and add weight to the exposed structure. The fouling load on carbon steel, stainless steel 304, Al 2 S and Al M57 S is about 16.0, 20.7, 21.6 and 21.9 kg per metre squared respectively in 5 months in the Cochin Harbour waters (Ravindran & Pillai, 1984). The fouling load destabilizes the oceanographic buoys and increases the frictional resistance to motion of ships and submarines causing increased fuel consumption for propulsion. It also results in significant hydrodynamic loading on offshore structures down to a depth of about 22 m (4) (5). Even minute level of fouling and corrosion is undesirable in the case of OTEC systems where it affects the heat transfer efficiency.

Corrosion and fouling adversely affect the sensors of oceanographic equipment by a combination of factors like increase in weight and hydrodynamic loading, impairment of electrical, optical and magnetic characteristics.

Of the several forms of corrosion which the metal may undergo, the galvanic attack, the pitting attack and the crevice attack are of much concern to the designers as they are less predictable in nature while in the case of uniform corrosion as in the case of corrosion of copper plates in unpolluted slow moving sea water, adequate corrosion allowance can be made in the design stage itself.

The corrosion and fouling behaviour of several metals in Indian harbour waters (De, 1968; Pillai & Ravindran, 1979) and in other parts of the world have been well documented (Scumacher, 1979). Typical pitting rates of some metals and alloys are given (Tuthil & Schillmoler, 1965) in Table 2.

Table 4 Typical pitting rates of metals and alloys in calm seawater (Velocity 1m.sec^{-1})

Material	**Resistance to Pitting**	**Typical rate of penetration in pits (Microns.year^{-1})**
High strength low-alloy steel	Fair	380-760
Low-carbon steel	Fair	380 – 760
Steel, with scale	Poor	510 – 1020
Cast or Sg iron	Good	100-300
Copper	Good	150 -300
Tin (40%) – Lead (60%)	Excellent	-
Brass (15 % Zn)	Good	150 – 300
Admiralty brass	Good (a)	150 – 300
Aluminium brass	Good (a)	180
Naval brass	Good (b)	180+
Aluminium bronze	Good	76
Nickel aluminium bronze	Good	50 – 230
Manganese bronze	Good (b)	250 – 380
Silicon bronze		180 – 360
Tin bronze	Good	130 – 250
Leaded tin bronze	Good	130 – 380
Nickel tin bronze	Good	20 – 50
90/10 Cu – Ni – Fe	Good	25 – 130
70 / 30 Cu – Ni – Fe	Good	25 – 130
59 % Ni – Cr – Mo alloy	Excellent	-
Ni – Cu Fe alloy 400	Fair (c)	130 – 380
Ni – Cu Fe alloy	Poor (c)	1530
Stainless steel type 304 L	Poor (c)	1780
Stainless steel type 316	Fair (c)	1530 – 1780
Alloy 20 (29 % Ni stainless steel)	Good (c)	180
Austenitic cast iron	Good	50 – 100

a Subject to dezincification unless inhibitors such as Sb, As or P are present

b Subject to dezincification which is reduced by presence of Sn

c At velocities of 5 ft/sec. (1.5 m.sec^{-1}), or greater, resistance to pitting is good –to-excellent and corrosion rates are less than 0.0001 in per year (25 microns.yr^{-1}) . Pitting rates may vary +/- 200%. These are typical of rates encountered when pitting occurs.

(To convert the corrosion rate from microns.yr^{-1} to mils.yr^{-1} multiply by 0.03937)

Galvanic effects

The designers should be extremely cautious while suggesting a combination of metallic materials on a single structure in view of the great intensification of corrosion of the anodic members of the structure. Galvanic corrosion occurs when two dissimilar metals are in electrical contact with each other and exposed to a common electrolyte such as seawater. The galvanic series La Que, 1951) and compatibility of fasteners (Thuthil & Shillmoller, 1965) given in table 3 and 4 provide a very useful guide as to which metal will undergo accelerated corrosion and which will receive protection when they are galvanically coupled in seawater, for example the coupling of carbon steel with copper will result in the increased corrosion of carbon steel and decreased corrosion (cathodic protection) of copper.

Table 5 Galvanic series of metals and alloys in seawater flowing at 4 m.sec^{-1} (Temperature about 25° C)

Material	**Steady-state electrode potential, volts (saturated calomel half -cell)**
(Anodic, corroded end)	
Zinc	-1.03
Aluminium 3003 – (H)	-0.79
Aluminium6061 – (T)	-0.76
Cast iron	-0.61
Carbon steel	-0.61
Stainless steel, type 430 active	-0.57
Stainless steel, type 304 active	-0.53
Stainless steel, type 410 active	-0.52
Naval rolled brass	-0.40
Copper	-0.36
Red brass	-0.33
Bronze, composition G	-0.31
Admiralty brass	-0.29
90 Cu – 10Ni – 0.82 Fe	-0.28
70 Cu – 30Ni – 0.47 Fe	-0.25
Stainless steel, type 430 passive	-0.22
Bronze, composition M	-0.23
Nickel	-0.20
Stainless steel, type 410 passive	-0.15
Titanium (a)	- 0.15
Silver	-0.13
Titanium (b)	- 0.10
Hastelloy C	-0.08
Monel 400	-0.08
Stainless steel, type 304 passive	-0.08
Stainless steel type 316 passive	-0.05
Zirconium (c)	-0.04
Platinum (c)	+0.15
(cathodic protected end)	

a Prepared by power – metallurgy techniques. Sheath compacted power, hot rolled, and sheath removed cold rolled in air.

b prepared by iodide process.

c From other sources

Table 6 Galvanic Compatibility of fasteners in seawater

Base metal	**Fasteners**							
	(1) **Al**	**C steel**	**Si bronze**	**Ni**	**Ni – Cr allyos**	**Type 304**	**Ni-Cu alloy 400**	**Type 316**
Al	Neutral	(2) C.	(2) Unsatisfactory	(2) C	C	C	(2) C	C
Steel & cast iron	NC	Neutral	C	C	C	C	C	C
Austenitic nickel cast iron	NC	NC	C	C	C	C	C	C
Copper	NC	NC	C	C	C	C	C	C
70/30 Cu-Ni alloy	NC	NC	NC	C	C	C	C	C
Nickel	NC	NC	NC	Neutral	(3) C	(3) C	C	C
Type304	NC	NC	NC	NC	(4) may vary	(3) neutral	C	(4) C
Nickel copper alloy 400	NC	NC	NC	NC	(4) may vary	(4) may vary.	neutral	(4) may vary.
Type 316	NC	NC	NC	NC	(4) may vary	(4) may vary	(4) may vary	(4) neutral

C Compatible, protected
NC Non-compatible, preferentially corroded
(1) Anodizing would change rating as fastener (1)
(2) Fasteners are compatible and protected but may lead to enlargement of bolt hole in aluminium plate
(3) Cathodic protection afforded fastener by the base metal may not be enough to prevent crevice corrosion of fastener particularly under head of bolt fasteners
(4) May suffer crevice corrosion, under head of bolt fasteners

Stainless steel

Stainless steel is a reliable structural material for the terrestrial applications and in seawater its corrosion resistance is not impaired by high water speed and turbulence. The corrosion resistance depends upon a thin oxide film that isolates the material from the environment. The film is quite resistant to fresh water and salt-water spray but when fully immersed in seawater the film is attacked by chloride ions. This makes the material susceptible to severe localised forms of corrosion such as pitting, crevice and inter-granular attack. This type of attack results in the formation of tunnels and holes. The best known SS used in marine engineering are type 304 and 316. These alloys are used for the manufacture of shafts, wire ropes, fasteners and condensers.

Table 7 Properties of 300 series SS in seawater

Type	Nominal composition (%)	Max. cont. immersion (months)
302	18 Cr, 9 Ni	4
303	18 Cr, 9 Ni, 0.15 S	Not recommended
304	19 Cr, 10 Ni	4
316	18 Cr, 12 Ni, 2 Mo	6

It is a wise practice to select readily available and proven materials such as plain carbon steel, brass bronze, cupronickels and non – metallic materials like teflon, acrylic, nylon PVC etc. Carbon steel is the most basic construction material for both static and floating marine structures. It is usually upgraded to more durable structural material. Stainless steel, filament wound epoxies though meet highly arduous service conditions in the sea they are less predictable in their performance and are more expensive. The use of such materials should be backed by expert advice. Detailed project engineering would need consideration on fatigue behaviour, weight of the final structure, the zone to which the structure is to be exposed, practicability of periodical maintenance, tolerable levels of corrosion and fouling and in certain specialized structures, information on physical, chemical and optic properties.

In the final analysis, it is logical to conclude that research efforts to develop improved materials will continue unabated and factors such as performance, efficiency and cost will be the principal guiding criteria for the designers.

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