Module 8

Corrosion Mechanisms Affecting Metals in the Marine Environment

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Contents

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1. Introduction

Many different metal alloy systems are used in a multitude of applications in the marine environment. Metal alloy strength, toughness and corrosion resistance is often critical in applications for sea going vessels and on/offshore structures if structural integrity is to be retained over the design life. For this reason it is important to know how to avoid the material structural and corrosion short comings in marine and seawater service. This knowledge also helps in identifying why unsatisfactory performance and failures in engineering components have occurred and what remedial measures should be considered to avoid and mitigate further risks.

The module is designed to acquaint the reader with the common material types used in the marine environment and how they can be undermined by corrosion. It is closely associated with Module 7 'Steels and Non-Ferrous Alloys in Marine Applications…' which deals with material designations, composition and mechanical properties. It is anticipated that a greater understanding of the way metal alloys can degrade in marine applications will help in more precise diagnosis of poor performance and component failure and further, provide a sound basis for considering the remedial measures that are most appropriate.

The module begins with fundamental aspects of corrosion processes including the main forms of corrosion before discussing the way in which ferrous and non ferrous materials can be undermined.

2. Marine Corrosion Fundamentals

All aqueous corrosion processes (corrosion in a wet environment) including those taking place in the marine environment are basically of an electrochemical nature, in which a metal reacts with its environment, in this case seawater. The corroding metal passes into the seawater as positively charged ions (oxidation or anodic reaction) which can be expressed by the following chemical reaction formula:

$$M \Rightarrow M^{n+} + ne$$

The ionisation of the metal releases electrons which participate in the balancing reaction in which electrons are consumed (reduction or cathodic reaction). Thus, the anodic and cathodic processes, both involving the exchange of electrons, occur at the boundary between the metal surface and the corrosive environment. Both processes can be visualised by the passage of electric currents through the boundary plane: from the metal to the solution in the anodic case and in the opposite direction for cathodic processes, see Figure 1. The cathodic processes most relevant in the context of corrosion are due to dissolved oxygen and hydrogen ions:

$$O_2 + 2\,H_2O + 4e \Rightarrow 4\,OH^-$$

and

$$2H^+ + 2e \Rightarrow H_2$$

The corrosion reaction of iron, for example, can be expressed chemically as follows:

$$2\,Fe \Rightarrow 2\,Fe^{2+} + 4e$$

$$O_2 + 2\,H_2O + 4e \Rightarrow 4\,OH^-$$

$$2\,Fe + O_2 + 2\,H_2O \Rightarrow 2\,Fe^{2+} + 4\,OH^-$$

This is a typical example of an electrochemical corrosion process in which the rate of anodic metal dissolution is balanced by the rate of cathodic reduction of dissolved oxygen at the metal surface, see Figure 1. The rates of both electrochemical oxidation (anodic) and reduction (cathodic) reactions depend in principle on temperature, concentration and potential. Generally higher temperatures and concentrations of the reacting species promote higher reaction rates. The effect of the potential is on the rate of electron exchange, increasing potentials leading to an increase of the oxidation rate and a decrease of the reduction rate. A decrease of the potential has the opposite effect. Theoretically it can be derived, as is found in many practical cases, that the logarithm of the current is linearly dependent on potential. In the corroding state the combination of metal oxidation and the concurrent reduction reaction proceed at the same potential, the free corrosion potential,

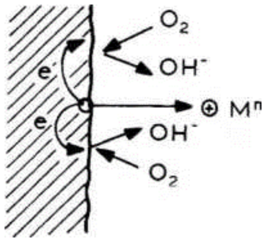

Figure 1. Schematic of the Electrochemical Process for Oxidation of a Metal and Simultaneous Reduction of Dissolved Oxygen[1]

Generally the following corrosion cases can be distinguished:

i) the corrosion rate is governed primarily by the rate of electron exchange at the metal surface and consequently by all factors which influence the value thereof, the potential being particularly important, as explained before;

ii) the corrosion rate is governed either by the supply of the constituent to be reduced to or by the transport of metal ions away from the surface; this case - which often applies to marine corrosion - is characterised by a strong dependence of the corrosion rate on the rate of transport in the solution (diffusion and convection);

iii) the corrosion rate can also be influenced by the electrical conductivity of the solution or of an insulating layer on the metal surface: the greater the resistance the lower the corrosion rate;

iv) a special case is passivity, where the metal surface is covered with a thin layer which acts as a barrier to the transport of ions and/or electrons, thereby lowering the metal oxidation rate to a very low value.

The electrochemical processes and the dependency of their rates on potential can be visualised by means of polarisation curves, which are an algebraic summation of the separate anodic and cathodic currents.

An important observation is that corrosion unlike mechanical strength is not a specific alloy property. In addition to the nature of the environment a number of other variables may influence the corrosion process in a quantitative as well as in a qualitative way (e.g. temperature, flow velocity, etc.). The dependency on so many variables which frequently interact with the corrosion process makes corrosion less easy to predict.

Another important distinction is between uniform and localized corrosion processes. The former applies to metal corrosion where the corrosion attack proceeds uniformly over the entire metal surface in contact with the environment, due to the conditions in the metal and in the solution being sufficiently homogeneous, Figure 2a. This is the most usual type of attack, the rates of which are generally fairly well known and therefore can be relatively easily incorporated in the design i.e, include a corrosion allowance.

On the other hand, in localized corrosion processes the oxidation of the metal proceeds at specific sites due to the presence of heterogeneities, Figure 2b. In a number of cases of localised corrosion the location of the attack is mainly determined by the metallurgical structure of the metal. Examples are intergranular corrosion and selective corrosion. In other cases constructional aspects of the structure may play an important part as for example in bimetallic corrosion, crevice corrosion, flow and/or stress induced corrosion.

Local corrosion processes can proceed on a microscopic as well as on a macroscopic scale. Generally the number of variables governing the rate of such localized processes is greater than with uniform corrosion, leading to increased uncertainty whether a localized process will proceed, and if so, at what rate. For this reason localized corrosion processes are more unpredictable and dangerous and as a small local perforation or a crack in a component can lead to outage of the whole system and thus their technological impact is larger[1].

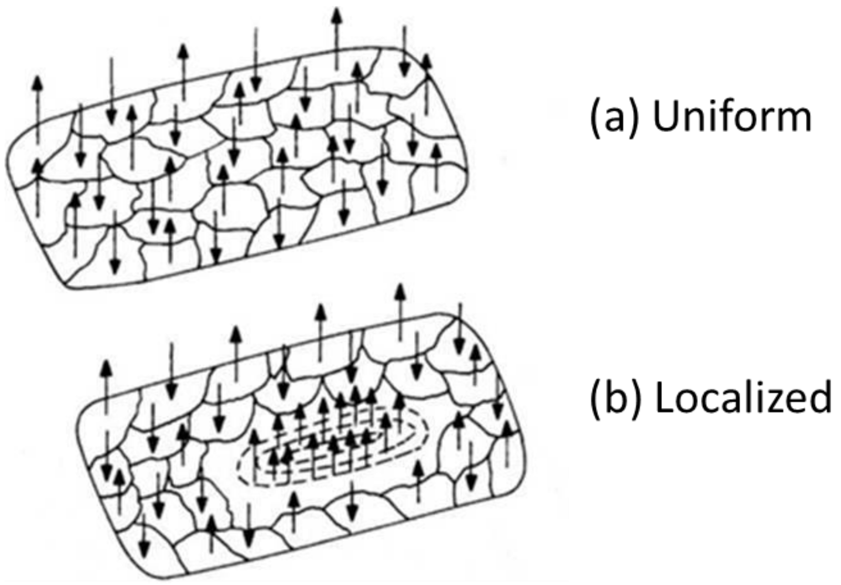

Figure 2. Schematic Representation of (a) Uniform Corrosion and (b) Localized Corrosion

In some cases the distinction between uniform and local attack is not very sharp. It is possible to distinguish several forms of localised corrosion, ranging from areas of shallow attack to the formation of very narrow and deep pits or cracks.

Factors which often play an important part in localized attack are:

- the cathode/anode area relationship
- differential aeration cells
- pH at the cathodic and anodic sites
- corrosion products or other layers present on the metal surface or formed during the corrosion reaction
- active-passive cells.

2.1 Cathode:Anode Area

It can be derived that the local attack will be more pronounced when the cathodic area is larger than the anodic area and when the rate of the cathodic process is higher, Figure 3. Under these conditions a larger cathodic current is available to support the anodic reaction. The balance between anodic oxidation and cathodic reduction is that between the electrical charge allied to these processes. When the anodic process is confined to a relatively small area a large anodic current density results, which is directly proportional to the corrosion rate and thus metal loss.

2.2 Differential Aeration Cells

Frequently a situation occurs where part of a metal surface is in contact with a solution in which oxygen is dissolved while another part of the same construction is in contact with the solution having a lower concentration of oxygen. Mostly such situations arise by limitation of the transport of the oxygen to different parts of the surface. It can be shown that at the surface which is in contact with the lower oxygen concentration, the corrosion rate when coupled to a surface in contact with a higher oxygen concentration increases as compared with the uncoupled state. In contrast, the opposite effect is observed for the surface in contact with the higher oxygen concentration on coupling.

2.3 pH changes during corrosion attack

In the majority of corrosion cases either dissolved oxygen or H^+ (acid) are involved in the corrosion reaction. In both cases the cathodic reaction involves an increase of the pH (i.e. decrease of acidity) at the metal surface, as can be deduced from eqs. 2 and 3. On the contrary the oxidation of the metal at the anodic site frequently leads to a decrease of the pH (acidification), for example by direct formation of H^+ during the electrode reaction:

$$Fe + H_2O \Rightarrow Fe(OH)^+ + H^+ + 2e$$

The actual change at the surface will depend on the solution chemistry (possible buffering action) as well as on the local flow conditions. However, it is clear that in cases where the anodic and cathodic sites are separated from each other (occluded cells: crevices, pits, cracks) locally substantial pH-changes can occur.

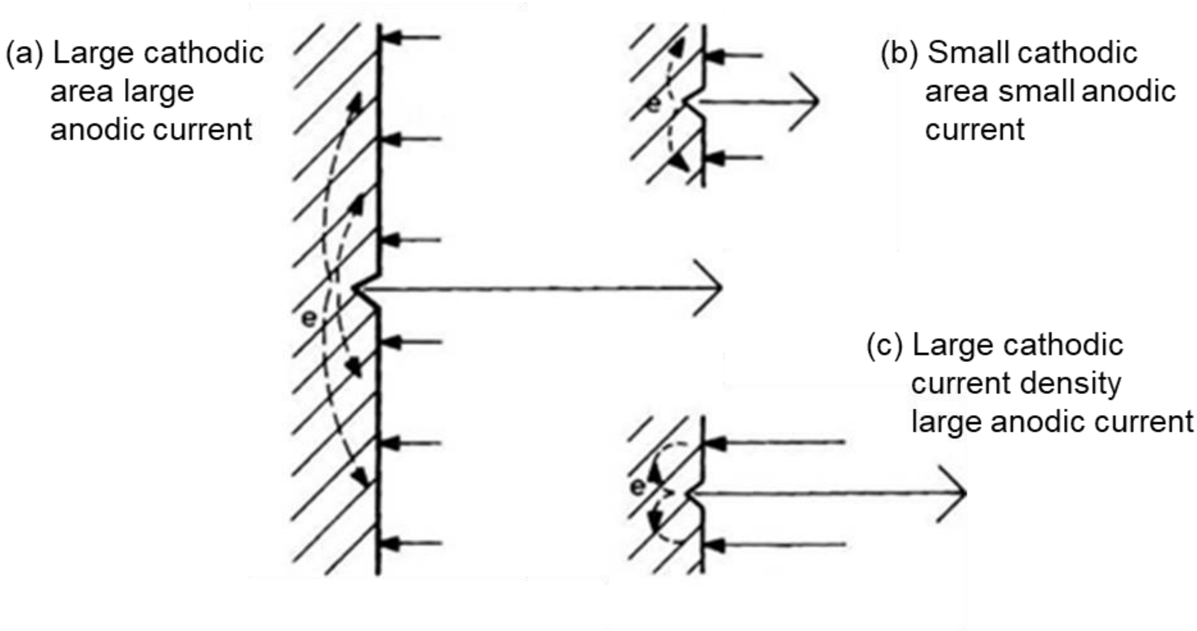

Figure 3. Schematic Showing that the Charge Associated with both Anode and Cathode are Equal, thus a larger Cathodic Surface gives rise to a Larger Anodic Current (a larger Corrosion Rate, c.f. (a) and (b)), as will a Larger Cathodic Current Density, c.f. (b) and (c) [1]

2.4 Corrosion Products and Deposits

When corrosion products or surface layers are present the formation of local cracks and pits in the layers can give rise to local corrosion at the base of these defects. A well-known example is mill scale on steel, in which cracks can develop due to different thermal expansion of the scale and the underlying steel. These cracks result in the formation of local corrosion cells, consisting of the bases of the cracks, i.e. the underlying steel surface, as the anodic sites and the mill scale surface as the cathodic site. When a deposit is present on a metal surface an anodic zone is often initially formed by a crevice between the deposit and the metal surface. Depending on the progress of the reaction the anodic zone may spread underneath the deposit.

2.5 Active-Passive Cells

When dealing with the corrosion aspects of passive alloys frequently situations occur when part of the alloy surface is in the desired passive state with low corrosion rate, while part of the surface has lost its passive state and has become activated (depassivated), and thus exhibits a much higher corrosion rate. A passive surface has the inherently higher corrosion potential and both surfaces are internally short-circuited through the metal. The effect of such an active-passive cell is to enhance the corrosion rate at the active part of the alloy surface. The magnitude of the enhancement depends on the ratio between the active and passive surface areas, the characteristics of the electrochemical reactions and the potential difference.

However, in many cases the above mentioned factors interact, which may complicate the understanding of the mechanism of localized corrosion.

3. Forms of Corrosion

Due to the many variables that initiate and drive the corrosion process many different forms of corrosion are found to occur. In general eight forms can be identified including,

- Uniform attack (or general corrosion)
- Pitting
- Crevice Corrosion
- Stress corrosion cracking (SCC)
- Galvanic corrosion (bimetallic corrosion)
- Intergranular corrosion (IC)
- Selective leaching (dealloying)
- Erosion corrosion

Other types such as corrosion fatigue, hydrogen embrittlement, cavitation arguably fall under one of these forms. The distinction in corrosion form is not always so clear, for example, crevice corrosion may begin as a series of distinct pits which ultimately coalesce to form a crevice and, pits act as stress raisers so may also initiate stress corrosion cracks i.e. different corrosion forms may occur in concert.

Classification by appearance (uniform or localized) is helpful as a preliminary method and is typically used in standard corrosion texts. However, it should be acknowledged that nomenclature to classify the different forms of corrosion types is not very logical. A number of corrosion forms are named according to the phenomenon which cause the corrosion, e.g. erosion-corrosion and crevice corrosion. In contrast other forms of corrosion are named according to their appearance after corrosion, e.g. pitting and intergranular corrosion. This inconsistency leads to the fact that in some corrosion types, e.g. erosion-corrosion, pits can be formed, although the corrosion effect is significantly different from classical pitting corrosion. In the following paragraphs those corrosion types, which are particularly prevalent in marine corrosion systems, is discussed.

3.1 Uniform attack

Uniform attack over large areas of a metal surface is the most common type of corrosion. According to the electrochemical mixed potential theory the anodic and cathodic sites are both distributed homogeneously over the metal surface (Figure 4). For this type of corrosion to occur it is required that the corrosion system exhibits no major heterogeneities, either in the metal microstructure and the environment (concentration differences) or in the exposure conditions (e.g. temperature differences, irregular flow patterns, local stresses). Large differences can be found between the uniform corrosion rates of different corrosion systems.

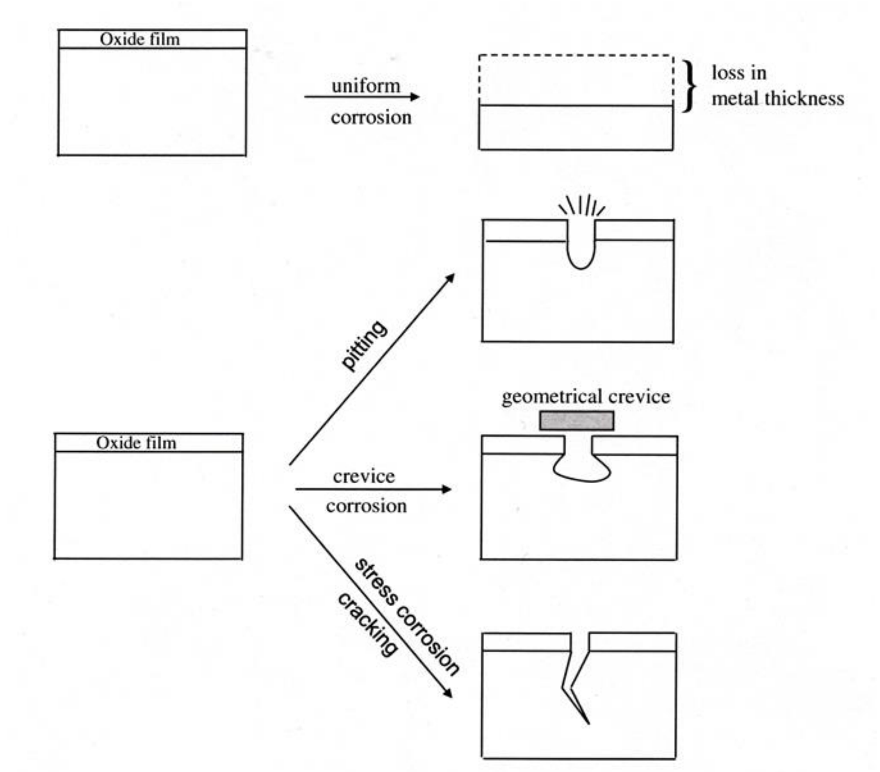

Figure 4. Schematic Representation of Uniform Corrosion and, Comparison with 3 forms of Localized Corrosion[2]

3.2 Bimetallic corrosion (galvanic corrosion)

This type of corrosion occurs when two (or more) dissimilar metals that are electrically connected to each other and are in contact with the same corrosive environment. In such cases the metal with the most negative corrosion potential in the uncoupled state (the active member of the couple) will show enhanced corrosion as compared with the corrosion rate in the uncoupled state but the other metal (the more noble metal with the higher corrosion potential in the uncoupled state) will corrode less on coupling, Figure 5. Dissimilar metals in the uncoupled state generally will differ in corrosion potentials and corrosion rates. In the coupled condition only one mixed potential can be attained which is situated between the original potentials of the separate metals.

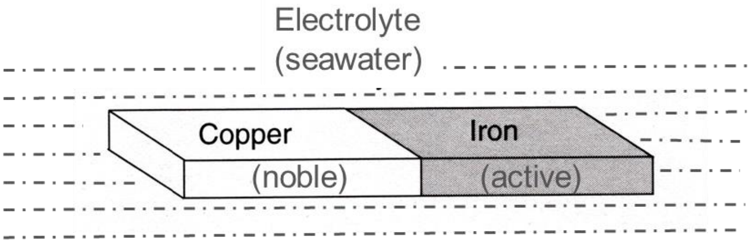

Figure 5. Two Metals in Contact Forming a Galvanic Couple[3]

For the active metal this means an increase of the potential, which is accompanied by an increase of the corrosion current, whilst the potential of the noble metal will be lowered and as a consequence so will the corrosion rate.

As in the case of differential aeration and active-passive cells a local current can be defined as the surplus current leaving the active metal and entering the more noble component at the metal-solution interface. Generally the following factors influence the bimetallic corrosion process:

- difference between the corrosion potentials of the uncoupled metals;
- electrochemical polarization characteristics of the metals in the vicinity of their corrosion potentials;
- electrical resistance of the bimetallic circuit, which can be attributed to the conductivity of the solution and/or corrosion products or paint films on the surface; the effect of the resistance is to lower the galvanic current;
- the surface area ratio of the cathodic and anodic region;
- geometrical considerations regarding the distribution of current across the boundary between the metals i.e. distance between the anode and the cathode.

Generally, a large difference in corrosion potentials, small slopes for the partial electrochemical reactions, a large ratio of the cathodic/anodic surface areas and a small distance between the metals will be detrimental. As a general guide of the possible effect of bimetallic corrosion tables are available, listing the corrosion potentials of separate metals and alloys in a given environment under specified conditions (galvanic series). As free corrosion potentials may depend on the chemical composition of the environment, galvanic series are pertinent to a given corrosive environment, for example, Figure 6 shows the galvanic series for seawater. However, it must be noted that in this particular case the free corrosion potentials of some classes of alloys, i.e. stainless steels, nickel-alloys and titanium, may become substantially higher in practical applications due to the formation of bacteriological slime layers. Also the free corrosion potentials may depend on factors such as flow velocity and temperature

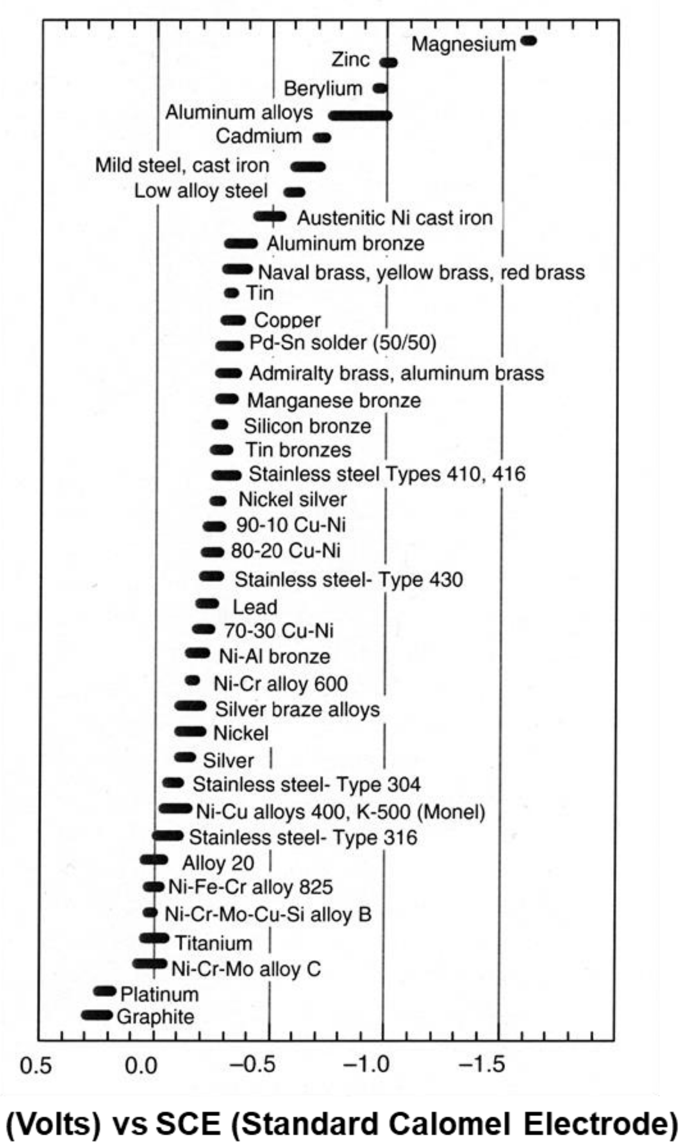

Figure 6. Galvanic Series in Flowing Seawater; Conditions 2.5-4ms^{-1}, Temperature Range 11-30^{o}C[1]

3.3 Flow-induced corrosion: Erosion-Corrosion and Cavitation

The effect of electrolyte flow is generally to enhance corrosion due to the improved mass transfer of ionic or solid anodic reaction products away from, or cathodic reaction species or intermediates to, the metal surface. Under laminar and uniform steady turbulent flow conditions the resulting accelerated corrosion is generally of a uniform nature, provided the diffusion layer is also uniform.

In many systems the corrosion rate will be limited by the mass transfer that may be involved in the anodic or cathodic partial reactions. However, with the higher flow rates associated with turbulence raisers, which are inevitable under real conditions, locally higher levels of turbulence are achieved giving rise to a localized corrosion termed erosion-corrosion. Apart from increasing the mass transfer process by the increased turbulence removal of protective layers of corrosion product may also occur, further accelerating the corrosion process. Moreover, if the corrosion potential of a corrosion product scale covered metal surface is more noble than that of the bare surface, the potential of the latter is increased, accelerating the anodic process still further, see Figure 7. If the electrolyte also contains entrained gas bubbles, which impinge against the metal surface at a specified location, the same kind of accelerating effect may be obtained, which is termed impingement attack. Impingement attack can also be associated with abrasion due to the impact of solid particles and is then termed erosion-corrosion or sometimes abrasion corrosion. Cavitation corrosion, which arises due to the collapse of vapour cavities or bubbles at a solid surface may also be classified within this group. Cavitation may give rise to material loss ranging from predominantly mechanical to predominantly electrochemical mechanisms. At low intensities of cavitation with vapour bubbles collapsing in the electrolyte the effect on corrosion may be the same as that due to impingement attack. However, at higher intensities of cavitation, bubbles collapsing on the metal surface may totally remove the corrosion product layer, while at even higher cavitation levels the forces exerted are sufficient to mechanically deform and erode the surface.

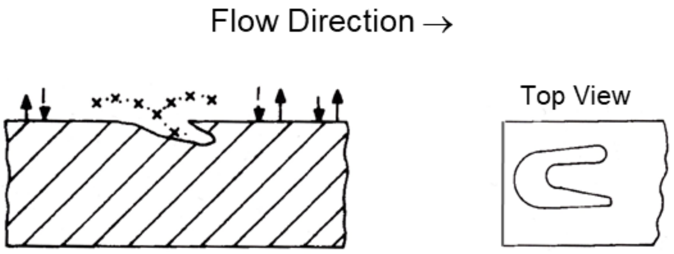

Figure 7. Erosion Corrosion and Horse-Shoe Attack[1]

Erosion corrosion is characterised in appearance by grooves, gullies, waves, rounded holes and valleys and usually exhibits a directional pattern. In particular with impingement attack a very specific pattern is observed, known as horse-shoe attack (Figure 7). The nature and properties of the protective layers that form on most metals and alloys are very important from the standpoint of resistance to the afore mentioned corrosion forms. The ability of these layers to protect the metal depends on the speed or ease with which they form when originally exposed to the environment, their resistance to mechanical damage or wear and their rate of reforming when destroyed or damaged. A hard, dense adherent and continuous layer would provide better protection than one that is easily removed by mechanical means or worn off. A brittle scale that cracks or spalls under stress may not be protective. Frequently the nature of the protective layer that forms, depends upon the specific environment to which it is exposed and this determines its resistance to erosion-corrosion by that fluid.

3.4 Crevice Corrosion

Crevice corrosion is a type of intense localized corrosion frequently occurring within crevices and other shielded areas on metal surfaces exposed to corrosive liquids, see Figure 8. This type of attack is usually associated with small volumes of stagnant solution caused by holes, gasket surfaces, lap joints, and crevices under bolt and rivet heads.

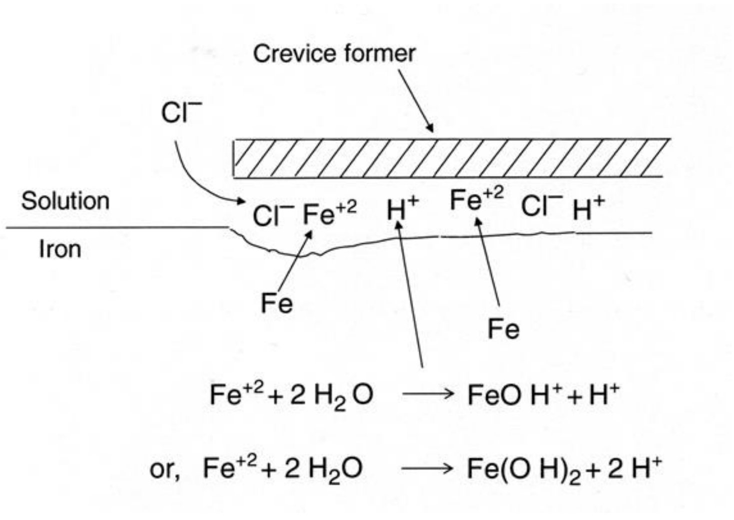

Figure 8. Schematic of Crevice Corrosion with Electrochemical Reactions for Iron

Crevice corrosion is characterised by a geometrical configuration in which the cathodic reactant (usually dissolved oxygen) can readily gain access by convection and diffusion to the metal surface outside the crevice, whereas access to the layer of the stagnant solution within the crevice is far more difficult and can be achieved only by diffusion through the narrow mouth of the crevice. For crevice corrosion to occur the crevice must be wide enough to permit entry of the solution but sufficiently narrow to maintain a stagnant zone of solution within the crevice, limiting the transport processes of diffusion and migration of ions. Solutions containing chloride ions are the most conducive to crevice corrosion. The mechanism of crevice corrosion is fairly complicated. The first step is the formation of a differential aeration cell due to cathodic reduction of dissolved oxygen within the crevice, access of fresh oxygen to the crevice solution being very limited. In contrast, the oxygen concentration at the freely exposed zone outside the crevice will be substantially higher. Due to the action of the differential aeration cell the anodic dissolution of the metal within the crevice will continue, resulting in the accumulation of positive metal ions within the crevice solution. The excess positive charge will be balanced, partly by positive ions migrating and diffusing to the outside, partly by diffusion of negative ions (CD to the inside. The net effect is an increase of the metal chloride concentration within the crevice, which on hydrolysis of the metal ions produces hydrogen ions:

$Fe^{2+} + 2\ H_20 \text{ -> } Fe(OH)_2 + 2H^+$

The $Fe(OH)_2$ is not protective, while the liberation of H^+ results in a decrease of the pH to values varying between 3 and 0.5, depending on the metal ions involved and the time elapsed. According to this mechanism an incubation period can be distinguished, necessary for the formation of a corrosive solution inside the crevice, characterised by almost zero oxygen content and high metal chloride and acid concentrations.

When this stage has been reached the anodic process within the crevice will proceed rapidly, which may be partly attributed to the direct reduction of H^+ inside the crevice. So the incubation period is followed by a propagation period, in which the rate of the anodic process frequently is seen to increase with time (autocatalytic process). In the case of stainless steels, which are particularly prone to crevice corrosion, the rate of the anodic dissolution is further accelerated by the relatively large driving potential which is formed between the outside of the crevice, which is passivated readily, and the inside which is depassivated by the aggressive crevice solution.

Corrosion processes which are closely related to crevice corrosion are deposit attack, in which a crevice is formed between a metal surface and a deposit (sand, mud, dirt), and filiform corrosion. The latter corrosion form is characterised by the formation of a network of threadlike filaments of corrosion products on the surface of a metal coated with a transparent lacquer or a paint film, as a result of exposure to humid atmosphere.

3.5 Pitting Corrosion

Pitting is a form of localised attack that may result in perforation of the metal, see Figure 8. These holes maybe small or large in diameter, but in most cases they are relatively small. Pits are sometimes isolated or so close together that they look like a rough surface. Generally a pit may be described as a cavity or hole with the surface diameter about the same as, or less than, the depth. Pitting is one of the most destructive and insidious forms of corrosion. It causes equipment to fail because of perforation with only a small percent weight loss of the entire structure. Pitting can often be ascribed to well-defined heterogeneities associated with the metal- environment system (e.g. discontinuities in mill scale, precipitates or protective layers). However, pitting can also occur in systems, which are apparently free from heterogeneities, provided aggressive ions such as Cl’ are present. Pitting corrosion occurs frequently at pores or damaged parts in:

- non-conductive layers on the metal surface;
- metallic surface layers which are noble to the base metal: bimetallic corrosion will occur, leading to pits in the base metal. In this latter case the pitting process can develop fairly rapidly, leading to deep pits within a short time.

Furthermore, undercutting of the metallic surface layer may occur under organic layers, e.g. paint; or corrosion product films and scales. Pitting is often promoted by the potential of the film covered surface being somewhat more noble than the bare surface.

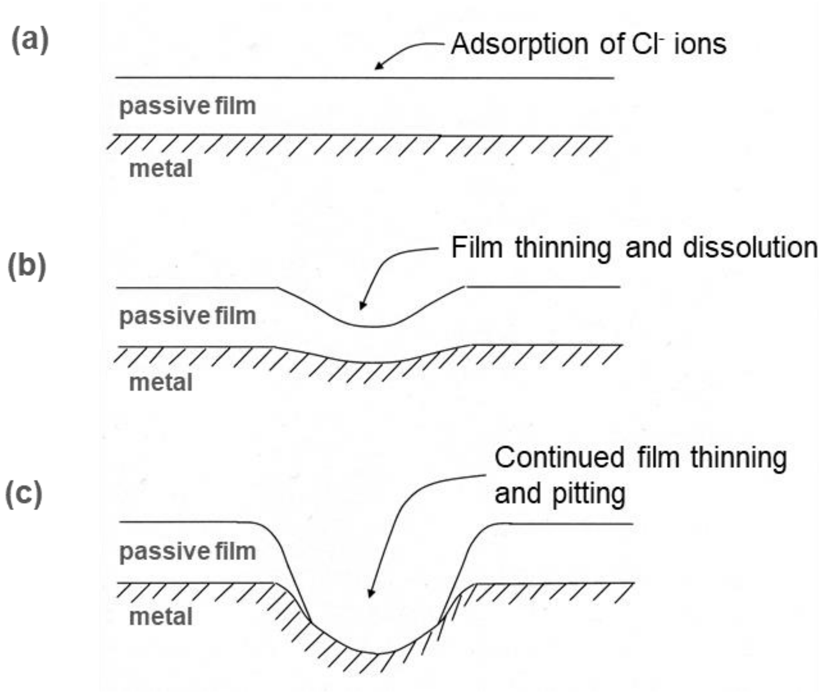

Figure 8. Passive Film Break-Down Mechanism for Pitting in which Chloride Adsorption Initiates the Process of Film Thinning eventually Leading to Pitting[2]

Pitting corrosion is often found with stainless alloys. Crevice corrosion and pitting of stainless steels have a number of features in common and it has been stated that pitting may be regarded as crevice corrosion in which the pit forms its own crevice. However, whereas a macroscopic heterogeneity determines the site of attack in crevice corrosion, the sites of attack in pitting are determined by microscopic or sub-microscopic features in the passive film.

Factors such as temperature and flow conditions will also influence the pitting mechanism to a great extent. At higher temperature the susceptibility of passivated alloys to pitting generally increases. Stagnant conditions will also be detrimental owing to the fact that the adverse solution conditions which develop in the micropit are not swept away thereby hampering a possible repassivation.

3.6 Selective Corrosion - Dealloying

In this corrosion form, which is also called selective leaching or parting, one element, generally the most active one, is selectively removed from a solid alloy, Figure 9. As a result the components of the alloy react in proportions which differ from their proportions in the alloy. Apart from the general term the process is often named after the removed element in specific cases, e.g. dezincification of brasses, dealuminification of certain Al-bronzes, etc.

A very well-know example of selective corrosion is dezincification of brass. Dezincification is readily recognized as the alloy assumes a red copper colour, i. e. in contrast to the original yellow. There are two types of dezincification: one is the uniform, or layer-type, and the other is the localised, or plug-type. The dezincified zones are mechanically weak and porous. Stagnant conditions (formation of deposits and scales), higher temperatures, low oxygen content and the presence of sulphides in the seawater generally will promote dezincification.

The metal structure and composition are also important: two-phase brasses are more susceptible than the single phase types.

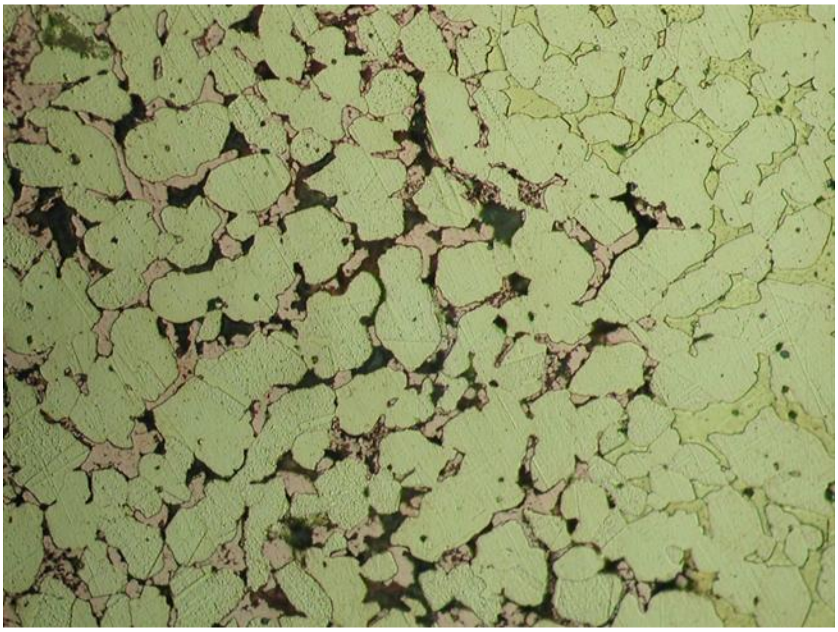

Figure 9. Microstructure of Dezincified Zone Showing Loss of Zinc Rich Phase (???) and Redeposition of Copper[1]

The susceptibility to dezincification of brasses can be decreased by decreasing the Zn-content (for example, red brass containing 15% Zn is almost immune). The addition of 1% Sn to 70-30 brass is advantageous (Admiralty Brass). Further improvement is obtained by adding small amounts of As, Sb or P to the alloy as inhibitor. However, such additions are not effective in high Zn (β-alloys).

Another alloy, which is well-known for selective leaching, is grey cast iron. In this case the interconnected graphite flakes are noble to iron, forming an excellent galvanic element on a microscopic scale. The iron is dissolved, leaving a porous mass, consisting of graphite, voids and rust. As a consequence the cast iron loses its metallic properties as well as its strength (graphitization). As in the case of brass, dimensional changes do not occur, and if not detected in time dangerous situations may develop.

3.7 Intergranular Corrosion (IC)

A metal is composed of crystals or grains. Generally the grain boundaries of the metal will show some enhanced reactivity, due to the local disordered structure. In many applications this is of little or no consequence, because the increase of reactivity relative to the matrix is only limited. However, under certain conditions grain interfaces will become very reactive and intergranular corrosion results, involving localised attack at and adjacent to the boundaries, with relatively little corrosion of the grains themselves. The alloy disintegrates (grains fall out of the matrix) and/or loses its strength, Figure 10. The main causes of intergranular corrosion are:

- impurities at the grain boundaries,
- enrichment of one of the alloying elements, or
- depletion of one of these elements in the grain-boundary area.

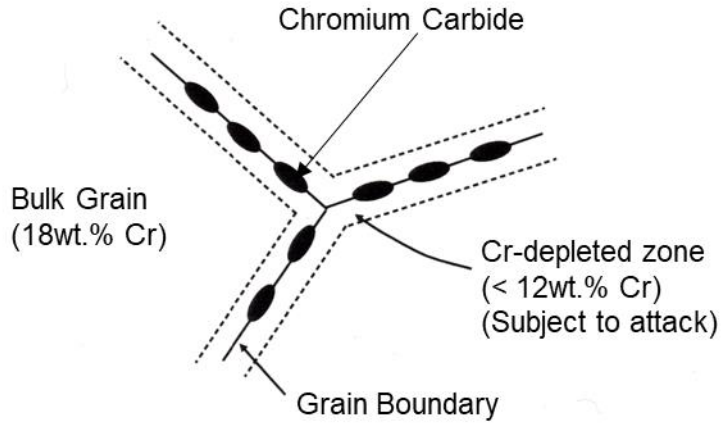

Figure 10. Schematic Representation of Sensitized Stainless Steel. Chromium Depleted Zones Adjacent to Grain Boundaries are Susceptible to Intergranular Corrosion[2]

A well-known example is the sensitization of austenitic stainless steel type AISI304 in the temperature range from 500 to 800°C. In this temperature range carbide precipitates, consisting of $Cr_{23}C_6$, are formed locally at the grain boundaries. The resulting effect is local depletion of chromium dissolved in the matrix. As the presence of dissolved chromium promotes the passivity of the alloy, the Cr-depleted grain-boundary zones will be susceptible to attack, because the dissolved chromium content locally is not sufficient to keep these zones within the passive range. On activation of the grain boundary zones active-passive cells will be formed, consisting of the grain surfaces in the passive and the grain boundaries in the active state. Due to the relatively large driving power of these cells and the unfavourable ratio of anodic/cathodic areas, rapid attack will be possible. A closely related phenomenon is weld-decay of austenitic stainless steels, which may occur after welding when the material adjacent to the weld is heated within the temperature zone in which sensitization occurs.

3.8 Stress Corrosion Cracking (SCC)

Cracks may be formed in many construction materials when they are exposed to a corrosive environment while a mechanical tensile stress is also present at a level which in itself should be not harmful. The cracks which are formed by this combined action are often difficult to detect and when allowed to grow may lead to sudden catastrophic failure, see Figure 17. In the SCC process two stages can be often distinguished: the first formation of the crack (initiation period) and the propagation of the crack (propagation period) ending with mechanical failure, resulting entirely from mechanical action on the reduced cross-sectional area. A necessary condition for SCC to occur is the presence of stress, which may arise from various sources, e.g. applied, residual, thermal. The environmental conditions for SCC to occur are rather specific, in the sense that not all environments promote cracking. Well-known materials which may show susceptibility to SCC in chloride environments are austenitic stainless steels containing Cr and Ni and a number of Al-alloys. Some copper alloys may be susceptible in the presence of ammonia. Cracking proceeds generally perpendicular to the applied stress. Both intergranular cracking, proceeding along grain boundaries, and transgranular cracking, advancing without apparent preference for grain-boundaries are observed. Intergranular and transgranular cracking also may occur in the same alloy, depending on the environment and/or the metal structure. Cracks can also vary in degree of branching. Generally the susceptibility to SCC increases with increasing temperature. For a number of alloy/environment combinations a safe temperature can be indicated, below which the susceptibility to SCC is practically nil. The progress of the SCC process under specified conditions of environment and stress level are also influenced by the potential. The interdependence of the variables in SCC, namely microstructure, electrochemistry and response to stress, support the suggestion that these interact in a variety of ways, leading to a continuous spectrum of mechanisms rather than a single mechanism.

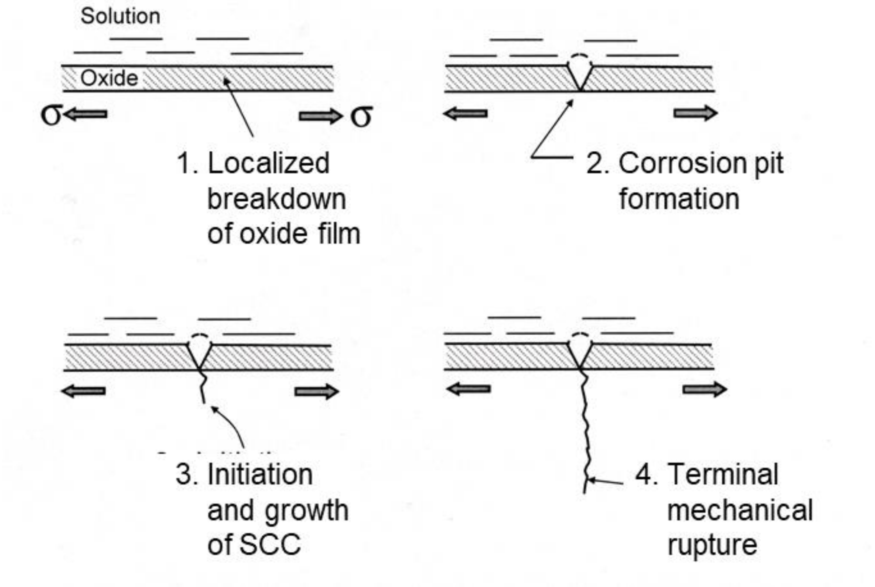

Figure 11. Stages in the Initiation of Stress Corrosion Cracks. Shaded Arrows denote the direction of the Applied Stress σ **[2]**

3.9 Hydrogen Embrittlement

High-tensile steels (low-alloy steels in which the strength is produced by suitable heat treatment) and, to a lesser extent, some high-strength alloys of copper, aluminium and titanium, are subject to SCC as a result of absorbed hydrogen. The phenomenon is so widespread as to constitute a special case of SCC, called hydrogen embrittlement. In addition to this there are many other cases of SCC, in which hydrogen is also thought to be involved in the reaction mechanism. It is apparent that for hydrogen embrittlement to occur hydrogen must be adsorbed at the metal-solution interface and that part of the adsorbed hydrogen must transfer across the interface to become absorbed by the metal. Hydrogen evolution and adsorption is favoured by low pH. It has been established that solution conditions inside a crack can be far more acid than in the bulk solution, which is ascribed to accumulation of metal salts (mainly chloride) and subsequent hydrolysis reactions in the crack. Possible sources of hydrogen in steel arise from such treatments as refining, welding, pickling, electroplating, phosphating and paint stripping. However, corrosion processes in which the corrosion reaction involves evolution of hydrogen, also arise. As stated above, even in the case of weakly - alkaline solutions such as seawater, the solution inside a crack may become strongly acidic with consequent discharge of hydrogen. In all these cases the uptake of hydrogen by the metal is promoted when the recombination of H to H_2 is poisoned (for instance by sulphur compounds). The application of coatings, which are more active than steel (e.g. Zn, A1 and Cd) may also be the cause of hydrogen embrittlement. The same applies to cathodic protection, either with sacrificial anodes or with an impressed current system.

3.10 Corrosion Fatigue

This type of corrosion is attributed to the simultaneous action of cyclic stress and a corrosive environment, resulting in cracks propagating from the surface in a direction perpendicular to the stress. Fatigue is often characterized by means of the relation between the amplitude of the cyclic stress (S) and the number of cycles before failure (N). In this way often a S-N curve is obtained, showing a critical value of the stress fatigue limit, below which no fatigue will occur, Figure 12. The influence of the corrosive environment is to lower the fatigue limit, sometimes even to zero. In addition the crack growth rate may increase.

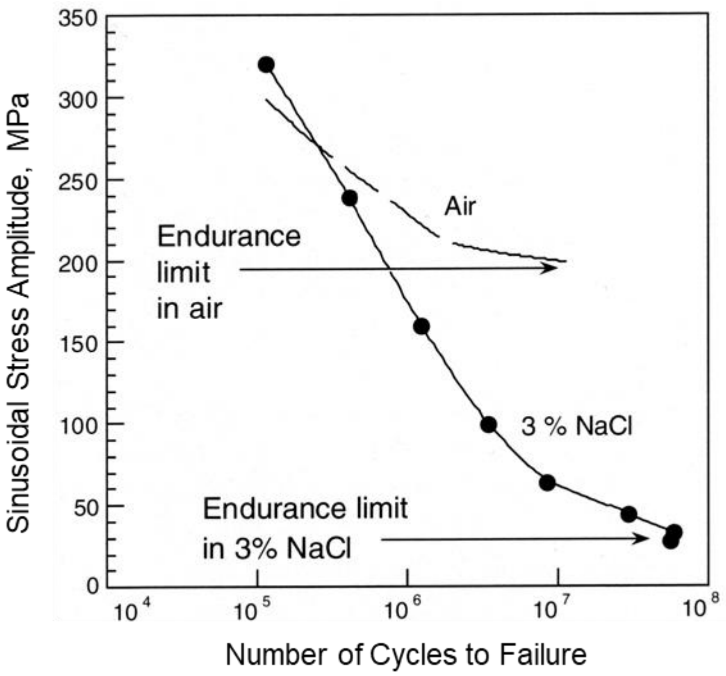

Figure 12. S-N Fatigue Curves for a 0.21wt. % C Steel in Air and in 3% NaCl[4]

Apart from the corrosivity of the environment, the frequency of the cyclic stresses are also important, low frequencies generally being more serious. As in the case of SCC and some other localized corrosion forms an initiation and a propagation period can often be distinguished, both periods being adversely affected by the corrosion reaction. As can be seen from Figure 13 cathodic protection may be effective in overcoming the detrimental effects of cyclic stresses although when applied to high strength alloys the possibility of hydrogen embrittlement should be taken into account.

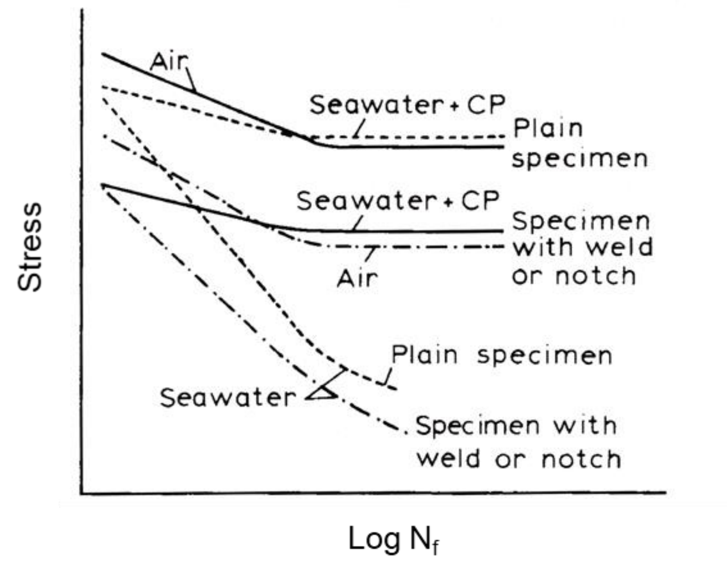

Figure 13. Schematic Showing the Effects pf Seawater and Cathodic Protection on S-N Curves of Steel

4. Corrosion Resistance of Metals used in Marine Applications

4.1 Ferrous Alloys

4.1.1 Mild Steel and Cast Iron

This chapter reviews the corrosion of carbon and low-alloy steels, as well as cast irons, in the uncoated condition. There are a number of coatings used with carbon steel to extend its life, but a discussion of these is outside the scope of this guide. Carbon and low-alloy steels are the most widely used materials in the marine environment, for both structural components and pressure-retaining applications. Table 1 lists some of the major applications.

Carbon manganese steels cover a range of compositions depending on the ductility and strength required. They are usually the lowest cost metallic materials. When ad-additional properties are required (e.g. higher strength, low-temperature ductility), small amounts of nickel, chromium, molybdenum, and copper may be added, either individually or in combination, to create special low-alloy steels. This guide does not propose to list all of the alloys here because they corrode in more or less the same manner in seawater.

Cast irons contain 2-4% carbon and the microstructure contains graphite as well as carbides. Ductile iron is the most common alloy, and it contains small additions of magnesium to spheroidise the graphite and increase ductility. In many respects, cast irons corrode similarly to carbon steels in seawater.

Austenitic cast irons contain 15-25% nickel and small additions of other elements. ASTM (A571)[5] UNSF43010 (Grade D-2M) is often used in castings for pump cases and valve bodies, as well as for centrifugally cast pipe. It has a lower corrosion rate in seawater than ductile cast iron, but it has a susceptibility to chloride stress corrosion cracking (SCC) in warm seawater (section 2.1.1.3.2).

Table 1. Typical Carbon Steel and Cast Iron Applications in the Marine Environment

Type	Alloy	Application
Structural	Carbon Steel and Cast Iron	Platforms, Jackets, Ship Hulls, Vessels, Piling and Sheeting, Towers, Bridges, Lock Gates, Gratings, Ladders, Cranes, Lifts and Loaders
Pressure Containing	Carbon Steel, Low Alloy Steels, Cast Iron and Austenitic Cast Iron	Piping, Pressure Vessels, Pumps and Valves

All carbon steels and cast irons corrode in aerated seawater, so they are low-initial- cost alloys, but have high maintenance/replacement costs unless protective measures are used. Offshore maintenance is very expensive and carbon steel is chiefly used with high quality coatings and/or cathodic protection (CP). When maintenance is simple and planned shutdowns are frequent, carbon steel may be a cost-effective option.

4.1.1.1 Marine Atmosphere

In marine atmospheres, the corrosion rate of carbon and low-alloy steels can vary from 0.01 to 0.1 mm year^{-1} depending on how close to the sea the exposed metal is located. In environments such as offshore platforms and ships' decks, where splashing is frequent, the corrosion rate is at the higher end of this range. Coupling to more noble (electropositive) metals can greatly increase the corrosion rate of carbon steel by galvanic corrosion at the junction to 1 mm year^{-1} or more. Corrosion of carbon steel leads to unsightly rust staining that may contaminate other equipment and cause accelerated attack. For example, corrosion products of carbon steel have caused localised pitting of 316L (UNS S31603) stainless steel.

Low-alloy steels generally perform similarly to carbon manganese steel. Carbon steel with ~0.5% copper is termed weathering steel, and in rural and urban areas, it can acquire an adherent and protective orange-coloured Film. However, in marine atmospheres, the copper has no protective effect; the corrosion rate is no lower than that of carbon steel and may be greater (in particular for non-rinsed applications)[6] .

There have been some recent developments in low-alloy steels for marine atmospheres. It is claimed that additions of silicon and aluminium give improved corrosion resistance to steels used for structures such as marine bridges over harbours[7].

In most cases in which carbon steels and cast irons are used in marine atmospheres, high-quality coatings are needed for a useful, low maintenance life.

4.1.1.2 Splash Zone

The intensity of corrosion of an unprotected steel structure in seawater varies markedly with position relative to the mean high and low tide levels. Protection of a steel structure can be achieved by various means. Each corrosion zone must be considered separately. Generally accepted methods are CP, coating, and sheathing.

The spray and splash zone above the mean high-tide level is the most severely attacked region because of continuous contact with highly aerated seawater, and the erosive effects of spray, waves, and tidal actions. Corrosion rates as high as 0.9 mm year 1 at Cook Inlet, Alaska, and 1.4 mm year^{-1} in the Gulf of Mexico have been observed[8]. CP in these zones is ineffective because of the lack of continuous contact with the seawater (the electrolyte), and thus no current flows between the metals for much of the time. Coatings need to be very robust as the conditions can be damaging. Sheathing with neoprene, other rubber coatings, or nickel and copper alloys has been used successfully.

Corrosion rates for bare steel pilings, etc., can also be high at the position just below mean low tide, and are caused by galvanic effects because of the different levels of aeration that occur in the tidal region. This can be controlled by CP systems because the metal is continuously immersed.

4.1.1.3 Submerged

In quiescent seawater, the general corrosion rate of carbon steel and cast iron is ~0.1 mm year^{-1}. However, cast iron and carbon steel can also undergo increased rates of corrosion under localised attack. General corrosion also increases as the seawater flow rate increases[9]. At a flow velocity of 4 m s^{-1}, the corrosion rate is approximately eight times that in quiescent seawater. Because austenitic cast iron contains nickel, it has a lower corrosion rate, typically 0.02 mm year^{-1} in quiescent seawater.

When steels and irons corrode in seawater, the corrosion rate gradually decreases because the corrosion products restrict diffusion of fresh water to the metal surface. For this reason, long-term corrosion tests (1 year or more) tend to yield lower corrosion rates than short-term tests.

When carbon steel is used as a sacrificial anode, fragmentation rather than general corrosion has sometimes been reported for high-carbon manganese and low-alloy steels. Mild steel ($C < 0.1\%$) has been found to corrode more or less uniformly as an anode, although alloys with $C < 0.15\%$ are also reported as satisfactory.

Over time, the matrix of cast irons gradually corrodes, whereby the metallic constituents are selectively leached or converted to corrosion products, leaving the graphite particles intact, and the surface is slowly enriched in graphite (graphitic corrosion). This causes the potential to become more noble (electropositive), and heavily corroded cast iron can become the cathode in a galvanic corrosion cell. This is a slow process in seawater and generally takes 10 to 20 years. It does not affect austenitic cast irons, because the corrosion rate is lower and components are not in service long enough for significant graphitic corrosion to occur.

Natural seawater (in contact with air) contains ~7 mg L 1 dissolved oxygen when saturated at approximately 20 °C, and this varies with temperature and depth[10]. In some cases, the seawater is deaerated, such as in multi-stage flash (MSF) desalination plants and seawater injection lines on offshore platforms. It is usual to express low levels of oxygen in parts per billion (ppb), where, for practical purposes, 1 ppb = 0.001 mg L

If the dissolved oxygen is maintained at <20 ppb, the corrosion of carbon steel is low. In most land-based plants, this can be achieved and maintained. Offshore, however, 50 ppb is a more common oxygen level and on some platforms, the control is so poor that levels of 100 to 500 ppb are not uncommon for extended time periods. Under these conditions, carbon steel develops significant corrosion.

The effect of dissolved oxygen concentration and temperature on the corrosion rate of carbon steel is shown Module ???, slide[11], These data assume that no protective films are formed. There is a sharp increase in the corrosion rate from 10 to 50 ppb 02, and thereafter, a more gradual increase from 50 to 200 ppb 02. The increase in corrosion rate from 10 to 80 °C at constant oxygen concentration is roughly the same order of magnitude as the increase produced by going from 10 to 50 ppb 02 at 10 °C. The results show the importance of keeping the dissolved oxygen content under control when carbon steel is used.

The use of galvanised steel pipe is sometimes suggested as an alternative to bare carbon steel, because it is readily available and is superior to bare carbon steel in fresh water. Galvanised steel offers no advantages in seawater because the zinc corrosion products are soluble. The zinc corrodes in a few weeks or months and then it acts just like bare carbon steel[12].

4.1.1.3.1 Pitting

Steels can undergo pitting to several times the depth of general corrosion under quiescent and flowing conditions. Hence, pitting corrosion is more likely to lead to leakage with carbon steel pipes[13].

4.1.1.3.2 Stress Corrosion Cracking

Carbon steel and cast irons do not usually develop SCC in seawater. Although austenitic cast irons have a lower general corrosion rate in seawater (~0.02 mm year^{-1}) than grey cast iron, they are susceptible to chloride SCC, particularly in warm seawater.

Traditionally, austenitic cast iron components have lasted for at least 10 years, even in warm climates like the Middle East. In recent years, however, failures of pump cases have occurred within 1 to 6 years[14]. The shortest times to failure were on as-cast parts, while stress-relieved parts lasted a little longer. This reduction in life probably results from commercial pressures, because castings used to be grossly over-designed, but with increasing pressure to reduce costs, wall thicknesses are being reduced, with a consequent increase in the stress at critical locations.

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increasing pressure to reduce costs, wall thicknesses are being reduced, with a consequent increase in the stress at critical locations.

4.1.1.3.3 Hydrogen Embrittlement

The normal potential of carbon and low-alloy steels in aerated seawater is about -550 mV SCE (saturated calomel electrode) and this is too electropositive to generate hydrogen. However, under the influence of CP, or coupling to more electronegative metals such as zinc, the potential can be -900 mV SCE or more negative, and hydrogen is then evolved. This does not cause a problem for most steels, but hydrogen embrittlement (HE) can occur with high-strength steels, such as those used for high- strength bolting or in jack-up rigs. This is avoided by using impressed current CP, low-voltage anodes, or Shottky diode limited conventional anodes, so the potential is about -850 mV SCE[16,17].

4.1.1.3.4 Biofouling and MIC (Microbial Induced Corrosion)

In natural seawater, carbon steel rapidly becomes covered with a thin fouling layer, followed quickly by attachment of shellfish and weeds. In some regions, this can happen very rapidly. In the Gulf of Mexico, a NPS 8 (200 mm nominal diameter) pipe became so full of fouling after 22 months that it had to be replaced[17]. Fouling of structures can also be severe enough to affect the mechanical loading.

When chlorine is added to the seawater to control fouling, this problem is eliminated, but there are increases in pitting and general corrosion as a consequence.

When flow rates are high, approximately 2 m s^{-1} and above, there is less likelihood of attachment of fouling, but this varies according to different geographical locations, partly because of the differences in seawater temperature, and partly because of varying microbiological activity. At low flow velocities, suspended matter may settle onto the tube; as a result, the region beneath the deposits quickly becomes anaerobic. This stimulates the activity of organisms such as sulphate-reducing bacteria (SRB). These well-known causes for pitting corrosion of carbon steel may cause penetration of a pipe wall.

4.1.1.3.5 Accelerated Low-Water Corrosion (ALWC)

The phenomenon of accelerated low-water corrosion (ALWC) was identified about 50 years ago and appears to be slowly spreading around the world. This is because there is a microbial involvement and it is thought that shipping may be spreading the bacteria involved in this form of attack[18].

ALWC affects sheet and tube piling and occurs between the mean low-water mark and the low astronomical tide mark. Corrosion rates can be 0.5 mm year 1 per side and because piling is normally installed uncoated, with a modest corrosion allowance, it is clear the life span of a piling can be drastically shortened.

The mechanism is thought to be a form of microbiologically influenced corrosion (MIC) and involves SRB becoming active beneath deposits and marine growths on the surface. The hydrogen sulphide can attack the carbon steel, but some can also diffuse into aerobic regions where sulphur-oxidising bacteria convert the hydrogen sulphide to sulphuric acid that further exacerbates attack of the steel. Although it is mostly seen on the seawater side of pilings, it can also occur on the landward side if there is sufficient seawater ingress and significant numbers of SRB[18].

A number of methods for combating ALWC have been tried, with the most successful being high quality coatings and CP. With piling, not all areas may be sufficiently protected by impressed current CP and a hybrid solution, combining both impressed current and sacrificial anodes, is required in some cases.

The whole phenomenon of ALWC, its causes and its prevention, has been reviewed and a document that includes an extensive bibliography was published by the International Navigation Association (PIANC) [18].

4.1.1.3.6 Galvanic Corrosion

When cast iron and carbon steel are coupled to most metals, the corrosion rate increases, whereas the level of corrosion decreases for the coupled metals. This is because of galvanic effects and the cast iron or steel becomes the anode. Because of their low cost, cast iron and carbon steel are frequently used as sacrificial anodes, for example, in the protection of brass tube plates in heat exchangers, and are purposely applied to corrode and decrease, or eliminate, the corrosion of the more vital component.

When cast iron corrodes, the graphite is left behind. Over a period of time, this means that the cast iron surface becomes soft and the component is much weaker. In addition, the graphite surface is highly cathodic to most metals, which can lead to accelerated galvanic corrosion of these metals.

4.1.2 Stainless Steels

4.1.2.1 Marine atmosphere

As chromium is added to carbon steel, the corrosion rate in a marine atmosphere decreases until at 12-14% chromium, the rate becomes difficult to measure. At 18% chromium and above, the weight loss is negligible. Ferritic stainless steels tend to show a surface rusting and shallow pitting that has little effect on section thickness but is not always acceptable aesthetically. Standard austenitic grades, for example, 316L (UNS S31603), can retain their bright appearance much longer, particularly when periodic washing down removes surface-deposit build-up, and superficial staining[19,20]. Higher-alloyed stainless steels also retain their bright appearance under more severe conditions.

The severity of marine atmospheric corrosion depends on several factors, notably the degree of salt deposition, which correlates with the direction of prevailing winds and distance from the surf, and the humidity. Because sea salt contains several constituents of varying hygroscopic tendencies, brine is present on the surface even under what would be considered ‘dry conditions’ - relative humidity as low as 50% at room temperature. Rainfall or cleaning can wash away the salt deposits and reduce the effect of marine corrosion. In structures, location and orientation strongly influence the extent of marine atmospheric corrosion, as shown in Figure 14.

Pitting and crevice corrosion can occur on 316L (UNS S31603) when used for hydraulic and instrumentation tubing. This was initially reported in the 1970s but its occurrence has increased during recent years. The problem is not limited to hot climates even though it is more common in subtropical and tropical areas. Field testing shows that 6% Mo and superduplex are successfully used in marine atmospheres as hydraulic and instrument tubing if the clamps are properly installed. Polymeric sheathing is another option that has been used with good results[21].

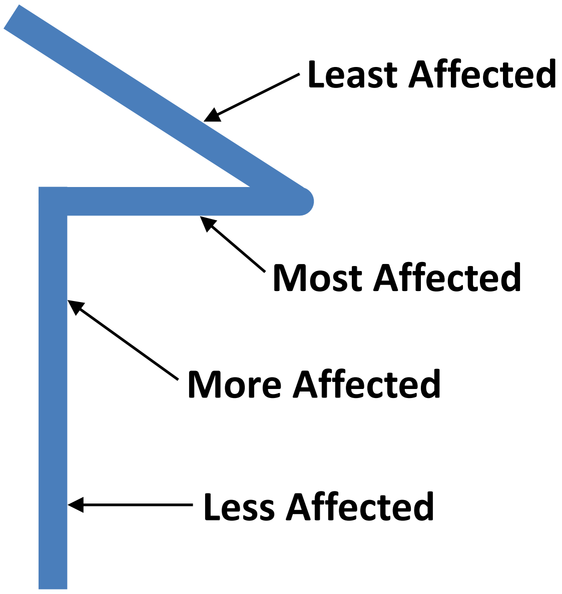

Figure 14. Schematic Showing Influence Location on Atmospheric Corrosion

For stainless steel subject to internal elevated temperatures, SCC can occur in the marine atmosphere and the following typical temperature limits have been applied: 50 to 60 °C for 316 (UNS S31600); 100 to 120 °C for 6% Mo; 80 to 100 °C for duplex; and 90 to 110°C for superduplex. It should be noted that the lower temperature limits are based on aggressive laboratory testing while the higher limits have been applied by end users without problems[22].

4.1.2.2 Submerged Conditions

Pitting of boldly exposed (non-creviced) base metal is an indication there are surface inclusions or imperfections in the metal, chlorination level is too high (as discussed later in this chapter) or the environment is too aggressive for the stainless steel grade, and a more resistant grade may be required. Pitting of stainless steels is usually seen in welds used beyond their service limits, or in the weld/heat-affected zone of poorly fabricated joints.

Typical areas for crevice corrosion are found beneath O-rings, flange faces under gaskets, threaded connections, nonmetallic connectors, tube-to-tube-sheet rolled joints, under adhesive tape, and under oxide scale. The tighter and deeper the crevice, the more severe it is. Such corrosion can also be found in quiet seawater conditions, normally at velocities less than 1 m s^{-1} when sediment or marine fouling is allowed to deposit.

Although the mechanisms for pitting and crevice corrosion are slightly different, they both involve localised oxygen depletion accompanied by metal dissolution, migration of chloride ions, and lowering of the local crevice pH. Crevice corrosion occurs more readily than pitting in seawater and at lower temperatures in the same bulk environment. Higher levels of the same alloying additions improve resistance to both types of corrosion.

Useful ranking of alloys is carried out by the pitting resistance equivalent number (PREN). See empirical formula below, or critical pitting or crevice temperature tests in ASTM G48[23].

$\text{PREN} = \%\text{Cr} + 3.3\ (\%\text{Mo} + 0.5 \times \%\text{W}) + 16 \times \%\text{N}$

The higher the values, the better the resistance to pitting and crevice corrosion. A PREN in excess of 40 is normally considered necessary for an alloy to be considered for aerated seawater[24,25]. Alloys with a low PREN number, for example, alloys 316L (UNS S31603) and 2205 (UNS S32205), usually require CP if not galvanically protected by other metals in the component or system[26].

When metal and environmental conditions are such that crevice corrosion is a possibility, attention should be paid to designing out crevices, for example, by avoiding threaded connections, sealing tight crevices with welds, and making full-penetration pipe welds. Alternatively, local improvements to crevice corrosion resistance are achieved at areas such as flange faces by weld overlaying with more resistant high-nickel alloys[27].

Biofilms form very quickly in seawater on metal surfaces and tend to give the stainless steel a more noble corrosion potential and increase the likelihood of initiation, and also the propagation of pitting and crevice corrosion compared with sterile water. Biofilm activity ceases at a temperature of 25 to 30 °C above normal ambient water than if the same water is heated to a temperature above which the bioactivity decreases significantly[28].

Chlorination, in optimal doses, is favourable to the corrosion performance of stainless steels in preventing fouling and marine growths that introduce tight crevices. For levels greater than about 0.1 to 0.2 mg L^{-1} free chlorine, the likelihood of crevice corrosion initiation increases[29]. The likelihood of crevice corrosion increases with rising temperatures in chlorinated water with no biofilm.

The highest chlorine level that can be used depends on the material and temperature. Norwegian experience suggests an upper temperature limit of 20 °C for superduplex and 6% Mo alloys with tight crevices (such as screwed couplings) with 1.5 mg L^{-1} chlorine[24]. Some companies have had better experiences with these alloys and permit use up to 30 °C or more for less severe crevices (e.g. flanged joints). The NORSOK[24] limit is considered over-conservative by some, and a combination of service experience and laboratory data indicates that maximum temperature is a function of chlorine concentration, as shown in Table 2.

In heat exchangers with seawater on the tube side and no crevices because the tubes are seal welded into the tube plate, the maximum operating temperature is restricted to about 60°C for superduplex and 6% Mo alloys even though the temperature at which pitting would be expected to occur is higher (~70 °C). This is because of the formation of calcareous deposits that start to appear at this temperature, and a ‘crevice corrosion’ type of corrosion that can occur beneath them[30], For higher- temperature service, calcareous scale deposition may be controlled through the use of complexing agents such as polymaleic acids or phosphonates. Sulphuric acid treatment is also frequently used. Such treatments must comply with pollutant discharge regulations and may be difficult to apply to once-through systems such as heat exchangers.

Stainless steels become more resistant to crevice corrosion if they are exposed to a less corrosive environment for some time before contact with a more aggressive environment[30,31], Thus, it is better to increase the chlorine value from zero to the nominal value over a couple of days, or start with intermittent chlorination. Alternatively, temperature can be used to aid film formation on piping located after a heat exchanger by using a regime such as the following.

1. Cold, natural seawater for 2 days minimum.
2. Cold, chlorinated seawater for 5 days minimum.
3. Hot, chlorinated seawater thereafter.

It is well recognised that the performance of welds can be improved by nitric/ hydrofluoric (HF) acid pickling, either by immersion, or using a pickling paste or gel[32,33].

Table 2. Suggested temperature limits for superduplex stainless steel in seawater at different chlorine concentrations[31]

Chlorine Concentration, mg/L (ppm)	Maximum Temperature, °C
0.7	40
1.0	30
5.0	20
200	10

4.1.2.2.1 Stress corrosion cracking

Chloride SCC is not a significant problem in seawater. If it occurs, it is usually in areas of high applied or residual stress such as expansion joints, bolting, or circumferential welds and/or areas where chlorides concentrate by evaporation on a hot metal surface. This includes conditions found in hot climates. Chloride SCC is essentially transgranular, frequently propagates from pits, and is unlikely to occur at temperatures below about 60 °C with austenitic stainless steels such as 316L (UNS S31603). More highly alloyed austenitic and duplex stainless steels do not usually develop chloride SCC below 100 °C.

In austenitic stainless steels, SCC is primarily related to nickel content. Type 300 stainless steels are the most susceptible grades. Alloys with 25% nickel are significantly more resistant than 316L (UNS S31603).

Duplex stainless steels, with mixed ferritic and austenitic structures, have a far greater resistance to SCC than the austenitic grades of similar pitting/crevice corrosion resistance. Ferritic grades with little or no nickel also have very high resistance to chloride SCC. The susceptibility of precipitation-hardened stainless steels to chloride SCC is a function of temperature and the strength level to which they have been aged[34].

4.1.2.2.2 Galvanic corrosion

Passive stainless steels are toward the more noble end of the galvanic series and are more noble than copper alloys, aluminium, and steel. Carbon steel and aluminium provide good protection to 316L (UNS S31603), but copper alloys do not provide galvanic protection[26]. The potential of stainless steels, high-nickel alloys such as Alloy 625 (UNS N06625) and alloy C-276 (UNS N10276), and titanium is similar, but graphite can be more noble and cause galvanic corrosion of stainless steels[28]. Galvanic corrosion tends to be lower in chlorinated vs. natural seawater[26].

The high density of inclusions in 303 (UNS S30300) and 303Se (UNS S30323), free machining grades of stainless steel, creates numerous galvanic cells in the material, these grades should not be used in seawater[20]. They can fail within 6 months even in contact with aluminium or steel. Graphite-containing gaskets, packing, and lubricants are all responsible for serious galvanic corrosion of stainless steel in seawater and should not be used[26], Information on the problems with gaskets and stainless steels, along with recommendations on suitable gaskets to minimise corrosion, is discussed in an article by Francis and Byrne[31]. If localised corrosion initiates in a stainless steel, the alloys become more active and, if the contact metal is nobler, the local corrosion rate may increase further.

4.1.2.2.3 Microbiologically influenced corrosion (MIC)

When initially immersed in seawater, most stainless alloys exhibit a corrosion potential of approximately 0 mV SCE. As microbes colonise the surface, its potential is ennobled, eventually rising to +250 or even +350 mV SCE. This electropositive potential may lead to crevice corrosion of lower-alloyed stainless steels. Although MIC is occasionally identified in lower-alloy stainless steels and particularly under extended stagnant conditions, it is not identified in practice in the more corrosion-resistant alloys (CRAs) such as 6% Mo austenitic or 25% Cr superduplex alloys[35,36]. The 6% Mo austenitic alloys are used in the United States in power stations to handle brackish water that has caused MIC in lower-alloy stainless steels. The U.S. Navy has also used 6% Mo alloys to prevent MIC in on-board cooling water pipes that alternate between flowing and stagnant conditions. Superduplex stainless steel piping was used with great success on an oil tanker in Australia to combat MIC.

4.1.2.2.4 Cathodic protection and hydrogen embrittlement

There are instances when stainless steels are present in systems for components that are cathodically protected. CP can be applied to less noble stainless alloys that do not have sufficient corrosion resistance in seawater, an example being to protect the seawater side of alloy 2205 (UNS S32205) subsea flow lines. Also, stainless steels can be present in a predominantly lower-alloy system in which the less noble alloys require CP.

When CP is applied, the rate of hydrogen production is negligible at potentials more positive than ~-800 mV SCE. At more negative potentials, hydrogen is generated on the stainless steel surface. This hydrogen may enter the metal and cause hydrogen embrittlement (HE) of some alloys. The likelihood is greater if the alloy is cold worked and under high mechanical stress. Austenitic stainless steel is better than duplex in resisting HE. Care has to be exercised in the design of CP systems and achieving optimum microstructures when duplex stainless steels are used. The Engineering Equipment and Materials Users' Association (EEMUA) guidelines describe the problem and provide advice on how to minimise the likelihood of HE of duplex alloys under CP[37]. Superferritic stainless steels are especially sensitive to HE caused by CP.

4.1.2.2.5 Good fabrication and installation practices

In addition to the factors already discussed, optimum performance from stainless steels, as with other materials, relies on control of the welding parameters, and attention to detailed design, plus good handling and fabrication practices[38]. The main objective of these welding parameters is to avoid crevices that could cause problems during service. The more important include:

- thorough degreasing is required before welding;
- marks from oil, crayons, sealant, sticky deposits (including stick-on labels), slag, arc strikes, and weld spatter should be removed;
- tooling, blasting, and grinding operations that can leave embedded iron or steel should be avoided; or, if unavoidable, a final nitric/HF pickling treatment should be used;
- correct selection of over-alloyed consumables for welding duplex and super austenitic; and
- inert gas back-purging is necessary during welding to minimise heat tint where formed, surface oxides and heat tint should be removed.

For tubular heat exchangers, crevice corrosion can be avoided if the seawater is on the tube side and not the shell side, and the tube is welded into a galvanically compatible tube sheet[39].

4.2 Non Ferrous Metals

4.2.1 Copper Alloys

4.2.1.1 Marine Atmosphere

Copper and copper alloys have a high degree of resistance to atmospheric corrosion. The resistance is a result of the development of a protective surface layer of corrosion products that reduces the rate of attack. When exposed to the weather, copper eventually develops a uniform green patina. Data from exposure tests[40] for up to 20 years in various marine sites examining a variety of copper alloys has found corrosion rates in the range of 1.3 to 26 x 10^{-4} mm $year^{-1}$. However, the corrosion rate was much higher for alloys susceptible to dezincification[41] Brass alloys can be susceptible to SCC when atmospheres are contaminated by ammonia, or closely related substances such as amines.

For galvanic couples in the atmosphere, copper is usually the cathode and can accelerate corrosion of steel, aluminium, and zinc. It is usually satisfactory when coupled with stainless steel[41].

4.2.1.2 Splash Zone

Metal sheathing has proved a very successful approach for preventing splash zone corrosion of steel structures and is applied to the region through the splash/spray zone to a short distance below the tidal zone. Two alloys predominate: namely 65/35 nickel-copper (UNS N04400) and 90/10 Cu-Ni. The former has been applied to the legs and risers of offshore structures for the past 50 years, and the 90/10 Cu-Ni was first used about 25 years ago in the Morecambe Gas Field, UK[42], Corrosion rates for both have been minimal.

The sheathing is normally welded into position as both alloys can be successfully welded directly to steel with appropriate consumables. Galvanic effects on the steel/ sheathing junctions are avoided on the lower end by CP on the steel structure and by coatings at the top of the sheathing in the atmospheric zone. When insulated from the steel (e.g. by neoprene or concrete), the copper-nickel can make full use of its biofouling resistance in the more submerged areas. Even with CP, the fouling is reduced, very loosely attached, and easily removed. Experience from the Morecambe Field, UK, where zinc anodes are applied to the legs, has found that fouling growth only reaches 25 mm. A good source of information and downloadable papers on this subject can be found at www.coppernickel.org.

4.2.1.3 Submerged

There are important differences in the corrosion characteristics of copper alloys in seawater but their general behaviour can be summarised as a low, general corrosion rate in quiet seawater with very little tendency to pit. They also have useful resistance to flowing seawater even at moderately high velocities. Care should be taken to avoid high flow rates and turbulence, as well as exposure to extended polluted conditions when ammonia or sulphides are present.

4.2.1.3.1 Passive Surface Layers

The corrosion resistance of copper and copper-based alloys in seawater is determined by the nature of the naturally occurring and protective corrosion product film that forms on their surface. These films can be multilayered and complex, and their compositions depend on the alloy group.

Protective surface films form by exposure to clean seawater over the first couple of days, but take longer to mature depending on the seawater temperature, and normally can take up to 2 to 3 months in European and North American waters[43]. Once established, the films can withstand intermittent levels of pollutants such as ammonia and sulphides.

The long-term, steady-state corrosion rate for copper and its alloys is on the order of 0.025 mm $year^{-1}$ or less and for copper-nickel alloys is 0.002 mm $year^{-1}$ within those flow velocities that each alloy can tolerate without damage to the protective corrosion product film. Long-term, steady-state corrosion rates provide a more accurate estimate of service life for copper alloys than data from short-term exposures.

4.2.1.3.2 Effect of Flow Conditions

The protective surface film that forms on copper alloys is resistant to flow until the shear stress from the flowing water is sufficient to damage it, leading to much higher corrosion rates. This critical shear stress, or breakdown velocity, varies from alloy to alloy and is also determined by the prevailing hydrodynamic conditions. Breakdown velocities in tube and piping are well understood, and various standards define maximum velocity limits for different bore diameters[44-46], The order of resistance for tube or piping is Cu < A1 brass < 90/10 Cu-Ni < 70/30 Cu-Ni < 2Mn-2Fe Cu-Ni < Cu-Ni-Cr. Of these, however, the 90/10 Cu-Ni (UNS C70600 [CW352H]) is the most commonly used alloy for seawater piping and heat exchangers having resistance that is sufficiently high to provide good service for many applications.

For geometries that have different hydrodynamics to tubing and piping, the breakdown conditions are less well defined. For example, a typical maximum flow rate within a 90/10 copper-nickel pipe at 100 mm diameter or greater is typically 3.5 m s^{-1}, but for a copper-nickel boat hull, speeds of 12 to 19 m s^{-1} have been successful without causing erosion-corrosion. Higher corrosion rates also are tolerable for intermittent flow in pipes. For instance, copper alloys are used very successfully in Firewater systems in which water velocities are typically 10 ms^{-1}. The reason excessive corrosion does not occur is because the system often is only in use for an hour or so per week and the surface film readily re-stabilises during the intervals.

In relative terms, copper, silicon bronze, and low-zinc brass alloys have the lowest resistance to erosion-corrosion; higher-zinc brasses are better, and copper-nickels and NAB have the greatest tolerance to higher-velocity seawater.

Castings such as gunmetals (copper-tin-zinc) and aluminium bronzes have good resistance to impingement (erosion-corrosion). Both groups are used for components such as pumps and valve bodies. NAB is also an established alloy for propellers as it has excellent resistance to cavitation.

At higher velocities up to 40 m s^{-1}, most copper alloys show a corrosion rate of approximately 1 to 2 mm $year^{-1}$. At this water velocity, severe impingement attack is experienced by all of these materials. Consequently, turbulence raisers, such as tight radius bends, partially throttled valves, and localised obstructions that can increase local water velocities by up to five times compared to the nominal flow, should be avoided for all copper alloys.

Minimum flow rates of about $1ms^{-1}$ are often included in tube and piping design to avoid sediment deposition that can interfere with heat transfer and lead to sulphide corrosion if sulphate reducing bacteria are present.

4.2.1.3.3 Selective Phase Corrosion

Copper-zinc alloys with more than about 15% Zn, such as naval brass and manganese bronze, are prone to selective phase corrosion in seawater. This is a form of corrosion in which the alloy is corroded and replaced by a porous deposit of copper. The rate of attack can be severe (e.g. 20 mm $year^{-1}$ in 60/40 brass), and because the copper deposit is porous and brittle, leakage may occur, for example, in condenser tubing and tube plates. This type of corrosion is called dezincification, and a similar effect is found in aluminium bronze above 9% aluminium (dealuminification). More rarely the effect is found in 70/30 copper-nickel and mostly at temperatures above 100 °C[41],

Brass alloys, single-phase alpha brass alloys can be rendered immune to dezincification by the addition of a small amount of arsenic (normally 0.02 to 0.06%) but this is ineffective in two-phase alloys such as 60/40 brass. However, in these alloys, the addition of 1% tin reduces the rate of dezincification considerably, and this addition is made in naval brass alloys. Therefore, when thick sections are used, as might be the case in tube plates with aluminium brass or copper-nickel heat exchanger tubing, acceptable lives can often be obtained from naval brass without any remedial action. Alternatively, dezincification in brass alloys can be avoided by using CP with iron or zinc anodes, or impressed current CP.

The addition of about 5% each of nickel and iron renders the duplex 10% aluminium bronze alloy more resistant to dealuminification, although the heat affected zone of weld in this material is susceptible in the as-welded condition. Specific heat treatments have been developed in NAB to avoid this.

Denickelification is very rare in 90/10 copper-nickel, and is also infrequent in 70/30 copper-nickel. A combination of low flow rates, deposits, high temperatures, and heat transfer in condensers favours the occurrence of this phenomenon causing thermogalvanic effects often referred to as hot-spot attack. The solution is more frequent cleaning to remove deposits that could lead to hot spots, and/or increasing flow rate to avoid deposits. A similar attack can occur at lower temperatures when ammonia is also present; ferrous sulphate dosing assists in its prevention when this is the case[41].

4.2.1.3.4 Pitting and Crevice Corrosion

Copper alloys do not generally suffer from pitting in clean, flowing water, although pits can occur in copper alloys from pollution, by sulphides generated in sediment, or deposits by anaerobic bacteria. While copper alloys are not subject to chloride pitting, heat exchanger tubes can pit if there are excessive residual carbon films in the bore from the manufacturing process; however, this is a rare occurrence with modern manufacturing methods[41],

Crevices can form at shielded areas under deposits and tight metal or non-metal contact areas such as under washers, O-rings, and flanged connections. In copper alloys, problems associated with crevice corrosion are rarely observed. This is because the mechanism is a ‘metal ion concentration cell’ effect with the area within the crevice becoming more noble than that surrounding it. This is very different from that associated with stainless steels as any resulting corrosion in copper alloys is mild and shallow in nature, occurs outside the crevice and is not temperature dependent.

However, aluminium bronze alloys in seawater can experience corrosion within the crevice[44] which is essentially a type of selective phase corrosion, and the degree depends on the phases present. NAB, which has a complex metallurgical structure[45], becomes susceptible when the pH drops within the crevice, turning the normally noble phase (kappa III) to one that is less noble than the surrounding alpha phase. This is insignificant if the surrounding exposed surface forms a protective film in aerated, flowing seawater at the outset, or the alloy is cathodically protected, or has sufficient galvanic protection from adjacent components[41-45].

4.2.1.3.5 Stress Corrosion Cracking

Ammonia and mercury are the primary causative reagents for SCC of copper alloys, which are essentially immune to chloride SCC as well as HE in seawater.

Brass alloys are the most susceptible to ammonia SCC[47]. In practice, SCC in brasses is more prevalent in marine atmospheres rather than under submerged conditions where very high levels of ammonia and stress levels are necessary for it to occur[41], If SCC is a possibilty, a stress relief anneal (280 to 300 °C) may be required. Cathodic protection (CP) can prevent SCC without risk of HE. Copper-nickel, copper-tin, and copper-aluminium alloys have a much greater ammonia SCC resistance[41]. Copper-nickels have the highest resistance, and the 90/10 and 70/30 alloys are virtually immune in seawater.

Although aluminium bronze is used satisfactorily in seawater, the matching weld filler metal can be susceptible to SCC in marine and desalination environments. The remedy is to weld with a higher, 10% Al, duplex filler metal and make a final pass with NAB filler to minimise the potential for galvanic corrosion. NAB propellers are routinely welded with NAB filler without increasing the susceptibility to SCC in service. Manganese bronze propellers can be stress-relief annealed after weld repair to reduce the likelihood of SCC.

4.2.1.3.6 Galvanic Corrosion

Copper alloys are central in the galvanic series of metals and alloys in sea water and generally compatible with each other unless area ratios are unfavourable. However, they are less noble than super stainless steels, titanium, and graphite, and this difference needs to be taken into account during design. Chlorination can make this effect less pronounced. Connection to less noble alloys or under CP can significantly reduce the biofouling resistance.

4.2.1.3.7 Polluted Seawater and Sulphides

If exposed to polluted water, especially if this is the first service water to come in contact with the alloy surface, any sulphides present can interfere with surface film formation, producing a black film containing cuprous oxide and sulphide. This is not as protective as films formed in clean water, and higher general corrosion rates and pitting can be experienced. The sulphide film can be gradually replaced by an oxide film during subsequent exposure to aerated conditions, although high corrosion rates can be expected in the interim. However, if an established cuprous oxide film is already present, then periodic exposure to polluted water can be tolerated without damage to the film.

4.2.2 Aluminium Alloys

4.2.2.1 Main Corrosion Types

Aluminium alloys in normal use corrode either by a mechanism involving general attack, or by a localised mechanism[48]. In seawater, provided the natural oxide film is maintained, general corrosion is rarely seen, as this type of corrosion mainly occurs when the environment pH is lower than 4 or greater than 8.5. Localised corrosion occurs in seawater because of a breakdown of the protective oxide film in isolated areas, and results in pits developing on the surface. The initiation of such pitting is a chemical attack by chloride ions at defective points in the passive oxide film[49].

Of the aluminium alloys available, the 5xxx alloys possess favourably high corrosion resistance in seawater[48,50], Generally, the 5xxx alloys are less prone to pitting corrosion than the 6xxx alloys. The presence of copper in aluminium alloys, such as 6061 (UNS A96061), produces deleterious cathodic defects in the oxide film. The detrimental effect caused by the presence of copper becomes even greater for 2xxx (Al-Cu) alloys; therefore, these alloys are not suitable for seawater applications. The high-strength 7xxx (Al-Zn) alloys also suffer from excessive corrosion in seawater and are rarely used in marine applications.

4.2.2.2 Other Corrosion Types

4.2.2.2.1 Crevice

Crevice corrosion is a particular form of localised corrosion and occurs when a crevice in a metallic joint allows a high concentration of chloride ions to develop, resulting in a breakdown of the passive oxide film. Examples of common crevice types are those found underneath a bolt head, gasket, or washer, or between a shaft and bearing. The occluded nature of the crevice allows low-pH environments to develop, which locally speed up the corrosion process. Crevice-type corrosion can also be stimulated by the presence of wet, porous insulating materials when they are in contact with aluminium surfaces.

4.2.2.2.2 Waterline

Waterline corrosion occurs just below the air-seawater interface on aluminium structures that are semi-submerged in seawater[51], It is more prevalent in stagnant conditions than those where the seawater is in motion. It is caused by the development of differences in chloride ion concentration when chloride ions become concentrated through evaporation at a stationary meniscus. A method of avoidance is to coat the area on either side of the air/seawater boundary.

4.2.2.2.3 Microbial Induced Corrosion (MIC)

Certain microorganisms can become attached to aluminium alloys from seawater or from contaminated fuel and give rise to slimy biofilms on the surface. These films can accelerate the initiation of pitting corrosion. Normal preventative measures are the use of coatings and biocides. Biofilm activity usually ceases at a temperature of 30 °C above the normal ambient temperature.

4.2.2.2.4 Galvanic Corrosion

Aluminium is a very reactive metal, and when placed in contact with another metal in the presence of moisture, an electrolytic cell is set up[52]. This situation could result in preferential attack of the aluminium, an effect known as galvanic corrosion. The driving force behind galvanic corrosion is the electrochemical activity difference between the two metals coupled together. Aluminium and its alloys are very electrochemically active, and when exposed to an electrically conducting medium (e.g. seawater), they tend to be the ones that corrode preferentially if any other metal is in contact. Carbon in contact with aluminium, most commonly found when incorporated in gasket materials, readily forms a galvanic cell and causes the aluminium to be preferentially attacked.

Normal methods of galvanic corrosion prevention are used, such as coating the surface of the more noble material (the cathode), electrically isolating the two metals, or applying cathodic protection (CP). The latter must be carefully designed because locally high pH values can be generated on aluminium at cathodic potentials, which can produce a breakdown of the passive film.

4.2.2.2.5 Intergranular Corrosion

Intergranular corrosion is a form of galvanic corrosion that takes place on a micro scale[53]. Some aluminium alloys can form almost continuous layers of very active intermetallic phases at grain boundaries if they experience certain thermal exposures (e.g. if non-ideal hot-working methods are used). 5083 (UNS A95083) is susceptible to this phenomenon, as precipitates of the MgAl, phase can form at the grain boundaries when the material is exposed to a temperature range of 65 to 200 °C.

Immersion of 5083 (UNS A95083) with severe grain boundary precipitation in a corrosive medium results in preferential attack of the material at the grain boundaries, producing intergranular corrosion. Thus, the maximum service temperature for 5083 (UNS A95083) is restricted to 65 °C.

Generally, 5xxx-series alloys with magnesium content lower than 3.5% are considered immune to intergranular corrosion. The 6xxx-series alloys do not normally display a susceptibility to intergranular corrosion.

4.2.2.2.6 Exfoliation Corrosion

Exfoliation corrosion is a specific form of intergranular corrosion that occurs on products manufactured in such a way as to make the grain boundaries prone to preferential attack[54]. Rolled or extruded materials are sometimes manufactured in such a way that the production process allows electrochemically active precipitates to form along the grain boundaries.

In this type of corrosion, intergranular attack progresses along the grain boundaries and the corrosion product, which has a higher relative volume than the original material, forces the grains apart, causing them to flake off. Because the resulting corrosion gives the separated grains an appearance similar to that of piles of leaves, the corrosion type has become known as exfoliation. This form of corrosion is particularly aggressive and causes a rapid decrease in cross-sectional area. In general, the only repair strategy involves cutting out the affected area.

Exfoliation corrosion is avoided by making sure manufacturing methods are fully controlled and product samples are tested before release. Standard accelerated test methods are available that stimulate exfoliation corrosion if a susceptible microstructure is present. ASTM G66[55] and ASTM G67[56] are the two most widely recognised test procedures.

4.2.2.2.7 Stress Corrosion Cracking

Stress corrosion cracking (SCC) can occur in some 5xxx- and 7xxx-series aluminium alloys if the alloy has a susceptible microstructure, particularly in cases in which the manufacturing process or subsequent thermal and/or mechanical exposure has allowed electrochemically active precipitates to form at the grain boundaries. Residual stresses in the material provide the required level of stress for cracking to occur. The 6xxx-series alloys are considered immune to SCC.

4.2.2.2.8 Corrosion Fatigue

Under cyclical loading conditions in the presence of seawater, the fatigue strength at 108 cycles of all aluminium alloys is normally reduced from that found in air by 25% to 35%. For a particular alloy, the corrosion fatigue performance is virtually independent of its metallurgical condition.

4.2.2.3 Design Considerations

The design of an engineering structure has a significant influence on its corrosion resistance. Therefore, design considerations can be made to reduce the likelihood of aluminium alloy corrosion in seawater. Some of these are as follows:

- Avoid contact between dissimilar metals as galvanic corrosion is a common cause of corrosion in aluminium structures. If contact is unavoidable, the surfaces should be electrically isolated from each other.

- Avoid crevices as these can be present in the design, but also occur as a result of weld defects, for example, where there are undercuts, lack of fusion, or partial penetration features. In areas where crevices cannot be avoided, the ingress of moisture should be prevented by applying coatings or sealants.
- Use continuous welding where possible. A continuous weld acts as a physical barrier to water ingress. Intermittent welding and riveting also result in the formation of crevices.
- Use good drainage systems. Corrosion can occur in stagnant water conditions. This is enhanced when water evaporates from the undrained seawater, increasing the chloride concentration. Pitting readily occurs under such conditions in all aluminium Avoid sharp bends in pipes, as these can result in erosion-corrosion of aluminium. The constant removal of the surface does not allow a protective oxide to form, and corrosion rates are enhanced.
- Avoid excessive stress concentrations, which can cause SCC and an increased rate of corrosion fatigue.
- Avoid sharp edges, which are an example of details that are difficult to coat in an effective manner. Components that are coated should be designed to provide the best coating condition.

4.2.3 Nickel Alloys

4.2.3.1 General Corrosion Resistance

Potential forms of corrosion in nickel alloys used in marine environments are pitting, crevice corrosion, and SCC. The level of resistance depends on the alloy composition and the severity of the environment.

4.2.3.1.1 Marine Atmosphere

In the marine atmosphere, Ni-Cu alloys generally have negligible corrosion rates, forming a grey/green surface film over prolonged atmospheric exposure.

Alloy 825 (UNS N08825) maintains a bright surface. Alloy 625 (UNS N06625) and the high-Mo, Ni-Cr-Mo alloys also essentially retain a bright surface and are unaffected by marine atmospheres.

4.2.3.1.2 Splash Zone

High corrosion rates of steel structures are found in the splash zone. Ni-Cu alloy sheathing is an effective means of avoiding corrosion in this area when applied from the splash/spray zone to below the tidal zone. Alloy 400 (UNS N04400) has been used as a splash-zone sheathing on steel platforms for more than 50 years, and for more than 30 years as a cladding on hot risers[57]. Corrosion rates of the sheathing are minimal. The sheet used is normally 3 to 5 mm thick and welded into position, although the alloy has also been used as metallurgically clad steel pipe for hot risers.

Galvanic corrosion of the steel below the sheathing is suppressed by the operating CP systems, and a properly maintained coating is required at the steel/sheathing interface in the atmospheric zone.

4.2.3.1.3 Immersed

Pitting and Crevice Corrosion

Pitting and crevice corrosion in Ni-Fe-Cr-Mo and Ni-Cr-Mo alloys normally require the presence of chlorides, as for stainless steels. They are also affected by pH, temperature, and tightness of the crevice. Crevice corrosion occurs more readily than pitting and at lower temperatures in the same bulk environment. Higher levels of chromium, molybdenum, and tungsten improve resistance to both types of corrosion.

Nickel maintains the austenitic-type structure so that high levels of molybdenum can be added while still maintaining a stable alloy. Thus, very high levels of resistance to localised corrosion can be achieved.

The pitting resistance equivalent number (PREN) is a means of comparing the relative resistance of alloys to both pitting and crevice corrosion, and for high-nickel alloys, it can be calculated from their compositions by the same formula as for stainless steels. However, nitrogen is not in use as an alloying constituent in nickel alloys because its solubility is too low in these alloy systems. Hence, the PREN for nickel alloys is calculated using the empirical formula below.

$$\text{PREN} = \%\text{Cr} + 3.3\ (\%\ \text{Mo} + 0.5 \times \%\text{W})$$

The higher the PREN, the greater the resistance to localised corrosion.

Ni-Fe-Cr-Mo alloys with a PREN < 40 (e.g. UNS N08825 and UNS N07718) can be susceptible to crevice corrosion in ambient-temperature seawater[58]. Galvanic or cathodic protection is required to ensure their resistance to crevice corrosion during seawater immersion. In polluted conditions when hydrogen sulphide is present, Alloy 825 (UNS N08825) has a better resistance to pitting than Alloy 400 (UNS N04400), which is known to be more susceptible under that condition[59],

Higher-molybdenum alloys 625 (UNS N06625) and alloy C-276 (UNS N10276) are substantially better and immune to corrosion in many severe marine environments. They retain extremely low corrosion rates in stagnant, flowing, and high-velocity seawater. Although subject to marine attachment, the alloys are highly resistant to crevice corrosion caused by such biofouling. Tight, deep crevices (e.g. sleeves) have occasionally initiated corrosion in alloy 625 (UNS N06625), but the higher alloys, such as alloy 59 (UNS N06059), alloy 22 (UNS N06022), alloy 686 (UNS N06686), and UNS N06200 (Ni-Cr-Mo-Cu), are very corrosion-resistant where extremely aggressive conditions are found. These alloys show little tendency to pit and crevice corrode even under many conditions of higher temperatures, chlorination, and low pH[60,61].

Nickel-copper alloys have been used for seawater service since the early 20th century and were initially considered resistant to pitting and crevice corrosion. This is now thought to be because they were usually the noble component in a mixed- metal system that provided them with galvanic protection[59]. When unprotected in quiet seawater, Ni-Cu alloys alloy 400 (UNS N04400) and K-500 (UNS N05500) can be susceptible to localised corrosion. Pitting tends to slow down after a fairly rapid initial attack, rarely exceeding 1.3 mm deep even after several years of exposure[58]. Connections to more noble high-alloy stainless steels, Ni-Cr-Mo alloys, and Ti can accelerate the localised corrosion of nickel-copper alloys. They can also pit in the presence of pollutants, such as hydrogen sulphide formed in stagnant, putrid conditions[59,60]. Low levels of chlorination (~0.5 mg L '), which eliminate the surface biofilm, can reduce the susceptibility to pitting. However, high levels of chlorination can cause pitting[59].

Stress Corrosion Cracking (SCC)

Type 300 series austenitic stainless steels are prone to chloride SCC at temperatures above -60 °C when under tensile (applied or residual) stress, and tend to fail in a transgranular manner (i.e. the crack grows through the grains in the metallic structure rather than around them). This can occur with minimal thinning, but can quickly and dramatically penetrate through the metal thickness.

Alloy 825 (UNS N08825) was developed to provide high resistance to chloride SCC compared to these low-alloy stainless steels, and, although it can fail under severe laboratory conditions, such as 42% magnesium chloride solution boiling at -154 °C, it is normally considered to have a very high resistance in the marine environment. Higher-nickel alloys of the Ni-Cr-Mo type and Ni-Cu alloys are not susceptible to this type of corrosion in seawater environments[58],

Flexible bellows are used for accommodating expansion and contraction of pipelines and ducts that commonly carry hot fluids, such as steam containing chloride impurities, and are a prime target for SCC. Readily fabricated alloys such as alloy 825 (UNS N08825) and alloy 625 (UNS N06625) are used for such purposes.

Under highly stressed conditions and CP, hydrogen embrittlement (HE) can occur when hydrogen charging occurs, reducing ductility and fracture toughness. Alloy K-500 (UNS N05500) bolting has been known to fail from this mechanism in marine service[61]. Alloy 725 (UNS N07725) and alloy 925 (UNS N09925) offer greatly improved resistance to HE[62]. More recently, cold-worked alloy 59 (UNS N06059) and alloy 686 (UNS N06686) have also been considered for fasteners to avoid HE.

Erosion Corrosion

Ni-Cu and Ni-Fe-Cr-Mo alloys have very good resistance to erosion-corrosion from fast-flowing seawater. In the presence of solids, the harder and stronger Ni-Cr- Mo alloys normally have better resistance.

Galvanic Corrosion

High-nickel alloys are noble and it is usually the alloy they are connected to that is likely to suffer from galvanic corrosion when area ratios are unfavourable.

Coupling Ni-Cu alloys to copper alloys and steels/cast irons is normally acceptable as long as the area ratios are not extreme; the galvanic protection offered to the Ni-Cu alloys can minimise localised corrosion. However, alloy 400 (UNS N04400) and K-500 (UNS N05500) are less noble than the Ni-Cr-Mo alloys and high- alloy stainless steels, and can develop localised corrosion as a result if connected to them [5,9], Ni-Fe-Cr-Mo alloys with a PREN < 40 can also develop pitting and crevice corrosion in seawater and this can be exacerbated if the material is coupled to a higher alloyed nickel alloy, or a high-alloy stainless steel in seawater (see section 4.1.2.2.2).

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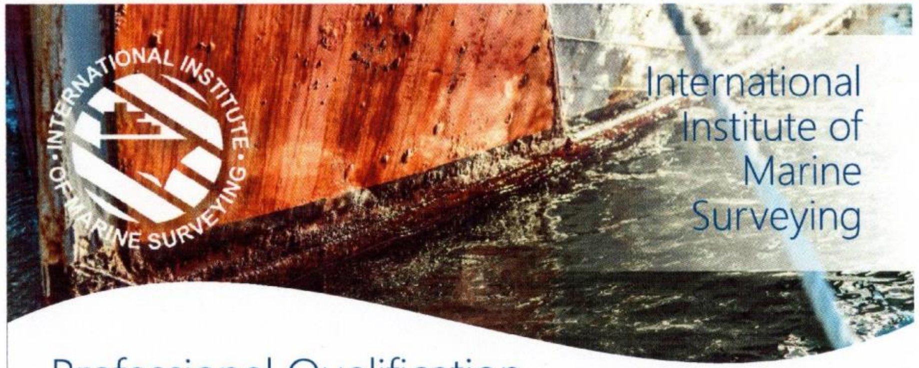
Module 8: Corrosion Mechanisms Affecting Metals in Marine Env.

INDEX (note pages: in black, corrosion mechanisms affecting metals in marine environment, slide nos. in blue; ‘a’, ‘b’ & ‘c’ refer to slide sections)

Part 2: Corrosion Mechanisms Affecting Metals in the Marine Environment

Section a	**Fundamental Principles and Forms of Corrosion**
Section b	**Corrosion of Ferrous Alloys**
Section c	**Corrosion of Non-Ferrous Alloys**



Professional Qualification in Marine Corrosion

Presented by **Mike Lewus**

Module 8

(section a)

Fundamental Principles and Forms of Corrosion

Module 7
(section a)

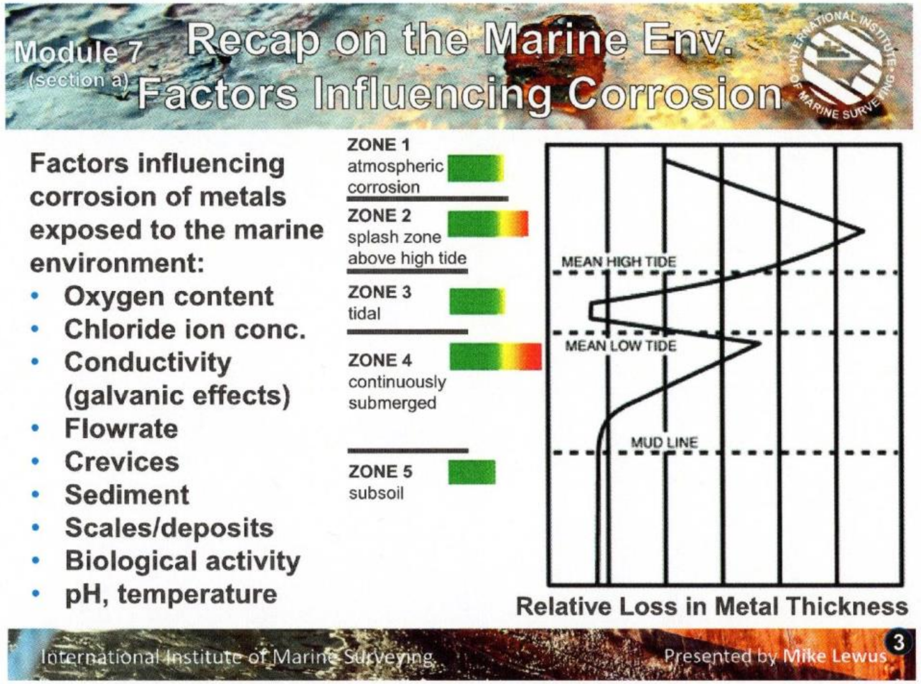
Summary

- Fundamentals
  - What is corrosion
  - Recap on seawater: factors that effect corrosion
  - Standard electrode potential and EMF series
  - Galvanic Series
- Pourbaix Diagrams & Evans Plots
  - Stability plots for Fe – water system
  - Stability plots for Au, Zn, Al
- Passivity in Metals
  - Passive metals and film destabilization
- Forms of corrosion
  - Uniform and localized
  - Galvanic (bimetallic) corrosion
  - Cracking phenomenon
  - Others: filiform, fretting corrosion, MIC etc.

Module 7
(section a)

What is Corrosion

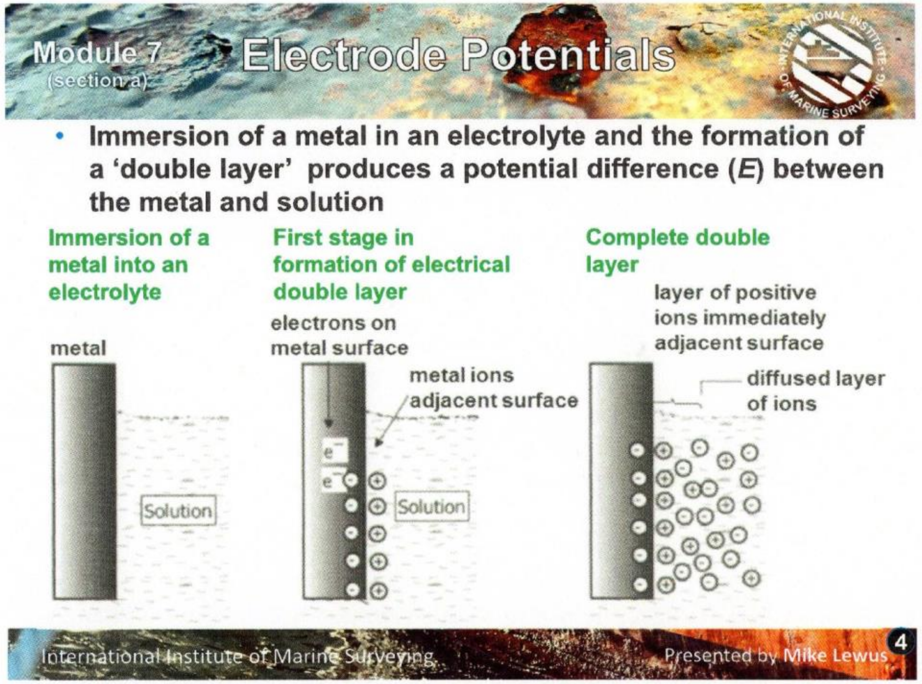
- Engineering metals extracted from ores are less stable than the ores from which they were extracted
- Exposure of these metals to the natural environment cause them to revert back to the ores from which they were extracted
- Corrosion is only possible if the products are more stable than the reactants i.e. there is a thermodynamic driving force for corrosion to occur
- If the change in Gibbs free energy (ΔG) during the transition of a system e.g. a metal being converted to an oxide is –ve then the reaction causing corrosion will occur spontaneously



Recap on the Marine Env. Factors Influencing Corrosion

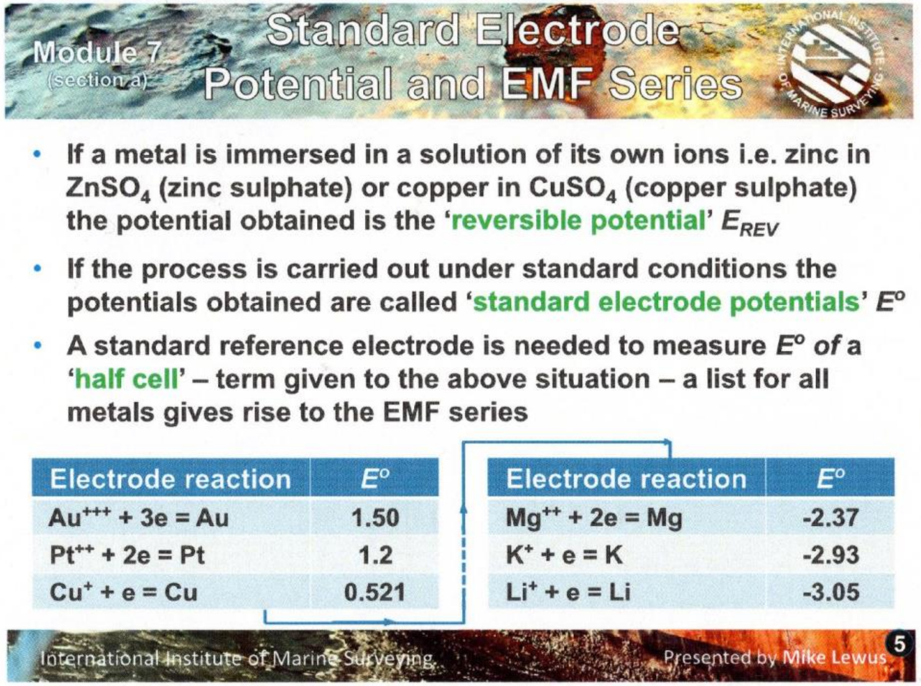
Factors influencing corrosion of metals exposed to the marine environment:

- Oxygen content
- Chloride ion conc.
- Conductivity (galvanic effects)
- Flowrate
- Crevices
- Sediment
- Scales/deposits
- Biological activity
- pH, temperature



Electrode Potentials

- Immersion of a metal in an electrolyte and the formation of a 'double layer' produces a potential difference (*E*) between the metal and solution

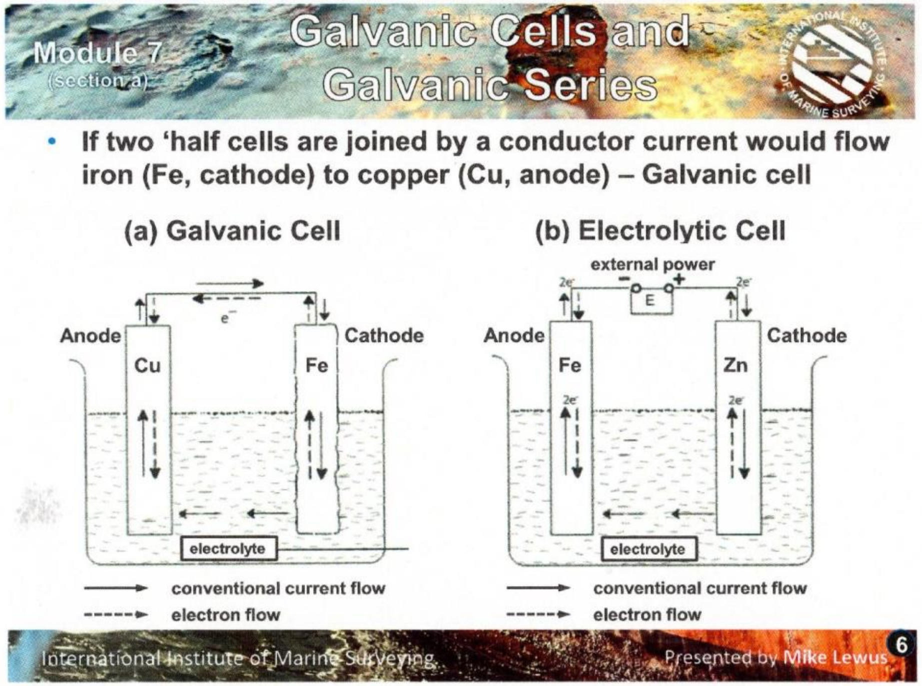


Standard Electrode Potential and EMF Series

- If a metal is immersed in a solution of its own ions i.e. zinc in $ZnSO_4$ (zinc sulphate) or copper in $CuSO_4$ (copper sulphate) the potential obtained is the 'reversible potential' E_{REV}
- If the process is carried out under standard conditions the potentials obtained are called 'standard electrode potentials' E^o
- A standard reference electrode is needed to measure E^o *of* a 'half cell' – term given to the above situation – a list for all metals gives rise to the EMF series

Electrode reaction	E^o
$Au^{+++} + 3e = Au$	1.50
$Pt^{++} + 2e = Pt$	1.2
$Cu^{+} + e = Cu$	0.521

Electrode reaction	E^o
$Mg^{++} + 2e = Mg$	-2.37
$K^{+} + e = K$	-2.93
$Li^{+} + e = Li$	-3.05



Galvanic Cells and Galvanic Series

- If two 'half cells are joined by a conductor current would flow iron (Fe, cathode) to copper (Cu, anode) – Galvanic cell

(a) Galvanic Cell

(b) Electrolytic Cell

Types of Corrosion Cell

- There are several types of corrosion cells
  - Galvanic cells
  - Concentration cells
  - Electrolytic cells
  - Differential temperature cells
- Galvanic Cell: has an anode and cathode of dissimilar metals in an electrolyte or, the same metal in dissimilar conditions in a common electrolyte
- Concentration Cell: Similar to galvanic cell except with an anode and cathode of the same metal in a heterogeneous electrolyte – concentration gradient
- Electrolytic cell: type of cell formed when an external current is introduced into the system

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Basic Wet Corrosion Cell: Electrochemical System

- Corrosion in the marine environment is wet corrosion - corrosion resulting from electrochemical reactions and presence of an electrolyte - in contrast to dry corrosion which occurs in the absence of moisture
- Essential requirements for a wet corrosion cell
  - Anode
  - Cathode
  - Ionic conductor (electrolyte/liquid conductor)
  - Metallic conductor (electrical connection)
- <u>At the Anode</u>; corrosion occurs by loss of electrons:

$$M = M^{z+} + ze^-$$

  - Anodic reaction, oxidation and electron production

Basic Wet Corrosion Cell: Electrochemical System

- <u>At the Cathode</u>; no corrosion - most important reactions
  - pH < 7 $2H^+ + 2e^- = H_2$
  - pH > 7 $2H_2O + O_2 + 4e^- = 4OH^-$

  Other cathodic reactions are possible!
  - Cathodic reaction, reduction reaction and electron consumption
- The anode & cathode in a corrosion cell must be in electrical contact
- The difference in free energies between the anode and cathode produces electrical potential which is the driving force for the corrosion reaction

---

Electrochemistry Principles

- **Electrochemistry:** the study of chemical processes that cause electrons to move
  - movements of electrons from one element to another occurs by oxidation-reduction ("redox") reactions
- **Oxidation:** reactions at an anode involve

  $Me \Leftrightarrow Me^{n+} + ne$
- **Reduction:** reactions at a cathode in acid solutions involve,

  $2H^+ + 2e^- \Leftrightarrow H_2$ **'hydrogen evolution'**

  $O_2 + 4H^+ + 4e^- \Leftrightarrow 2H_2O$ **'oxygen reduction'**

& reactions at cathode in neutral or alkaline solutions involve

$O_2 + 2H_2O + 4e^- \Leftrightarrow 4\,OH^-$ **'oxygen reduction'**

$Me^{+++} + e^- \Leftrightarrow Me^{++}$ **'metal ion reduction'**

$Me^{++} + 2e^- \Leftrightarrow Me$ **'metal plating'**

Faraday's Law and the Nernst Equation

- Arguably the most important laws in corrosion science are Faraday's laws &, Nernst Equation
- Faraday's 1st law - the mass of primary products formed at an electrode by electrolysis is directly proportional to the quantity of electricity passed

$$m \propto It \quad \text{or } m = ZIt$$

where I is current (A), t = time (s), Z = constant

- Nernst equation:

$$E - E^{O} = \frac{RT}{nF} \ln \left[\frac{a_{M_1} a_{M_2^{n+}}}{a_{M_2} a_{M_1^{n+}}} \right]$$

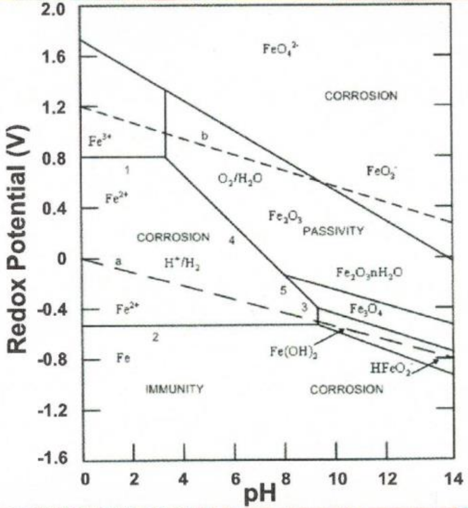
where a_{M_1}, a_{M_2} activities of metals 1 and 2, n = no. of electrons, F = Faraday constant, R = gas constant

Porbaix Diagrams: Stability Plots

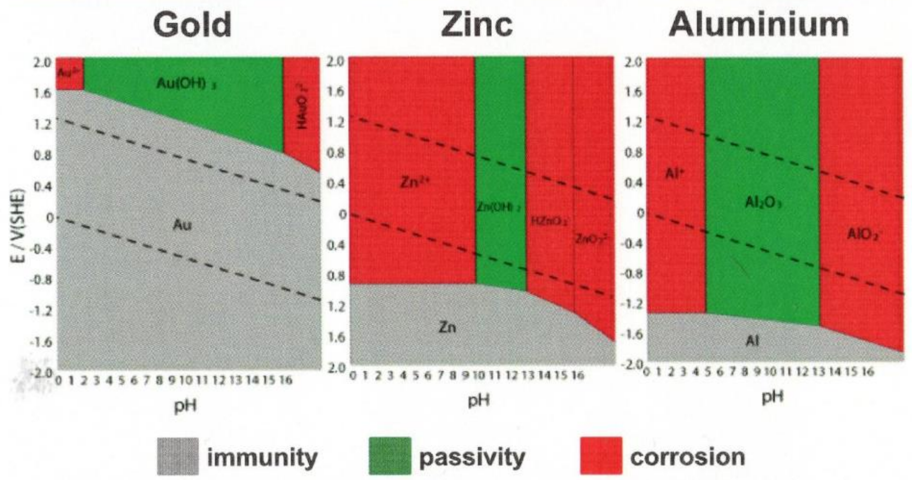
- Pourbaix diagrams are Potential-pH plots named after their originator Marcel Pourbaix, a Belgium corrosion scientist
- Pourbaix diagrams are analogues of phase equilibrium diagrams showing where a phase is stable at a particular combination of pH and potential
- pH is plotted on the horizontal axis and redox potential E (vs SHE) on the vertical axis
- Horizontal lines represent electron transfer reactions – they are pH independent, but potential dependent
- Vertical lines are not accompanied by electron transfer – they are potential independent but pH dependent

Porbaix Diagrams: V versus pH for Iron

- Diagrams are calculated for equilibrium conditions at 25°C
- The concentration of all metal ions is assumed to be 10^{-6} mol/litre – at lower concentration corrosion should not occur
- The upper end of the redox potential axis is the noble end, the lower end is the active end i.e. oxidizing power increases with increasing potential



Pourbaix Diagrams: Gold, Zinc and Aluminium



Passivity in Metals

- **Definition of Passivity:**
  The reduction in chemical or electrochemical activity of a metal due to the presence of a protective surface oxide film
- **Transition metals (Fe, Cr, Co, Ni, Mo) and their alloys (Fe-Cr stainless steels) tend to have very thin passive films which are 10's to 100's of angstroms (1-10nm) thick**
- **Non transition metals (Zn, Cd, Cu, Mg, Pb) tend to have much thicker passive layers which can be 1000's to 10,000s of angstroms (100 – 1000 nm) thick**
  e.g. passive film on copper pipe in water systems consists largely of Cu_2O with a thickness ~500nm

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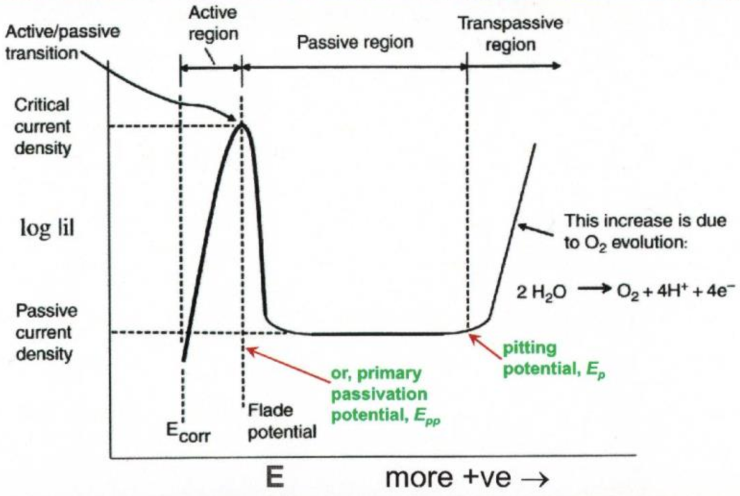
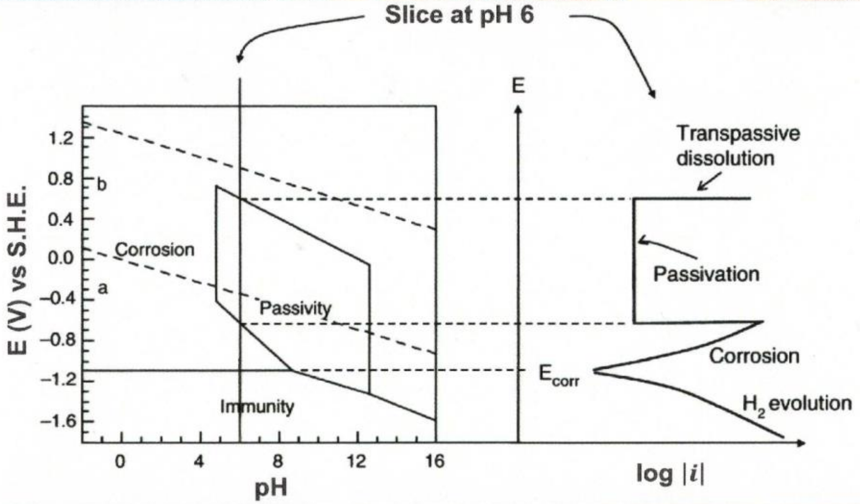
Polarization Plots: Passivity, E_{pp} and E_p



Correlation Between Pourbaix & Polarization Plots

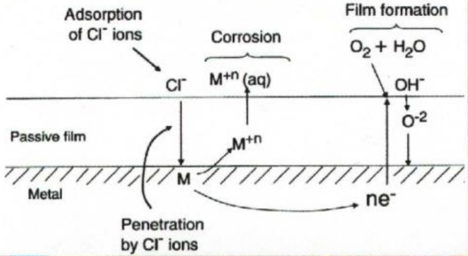


Key Elements of Polarisation Plots

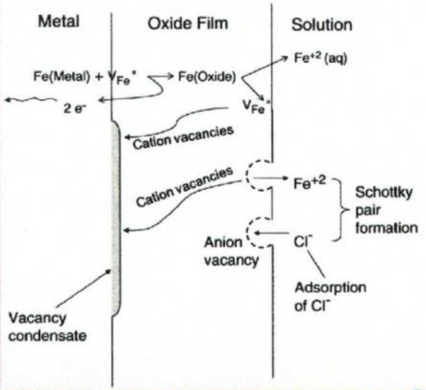
- **Polarization plots show the change in electrode potential due to the flow of a current**
- **The plots highlight:**
  - **Anodic polarized region: the displacement of the electrode potential in the positive direction so that the electrode acts more anodic**
  - **Cathodic polarization region: the displacement of the electrode potential in the neative direction so that the electrode acts more cathodic**
  - **The plots are a benefit because they can be used to determine**
    - **E_{pp} the primary passivation potential**
    - **E_p the pitting potential**
    - **Extent of passive region and breakdown conditions**
    - **Corrosion rate i_{corr} for a particular media/solution**
    - **Effect of changes in concentration of aggressive ions i.e Cl^-**

Passive Layer Breakdown Mechanisms

- **Penetration mechanism for pitting: competing processes of passive fim rupture and film formation**
- **Aggressive ions are transported through the passive film to the metal substrate and cause dissolution at the interface**



- **Cation vacancies are transported inwards and chloride ions are adsorbed at anion vacancies**

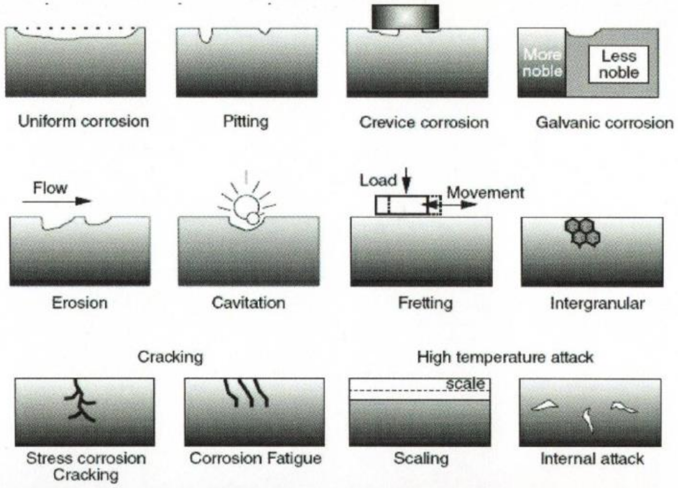


Additional Slides: Forms of Corrosion

Forms identifiable by visual inspection - but what don't we still know?

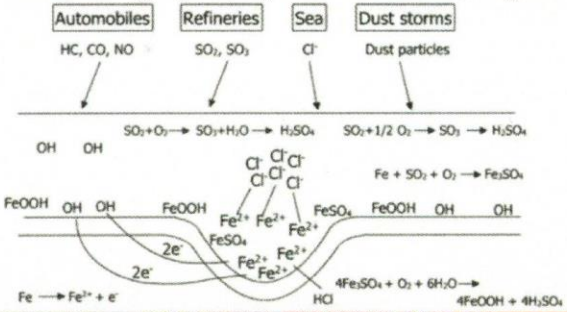
Forms identifiable using special inspection tools

Forms identifiable by microscopic inspection



Additional Slides: Uniform Corrosion

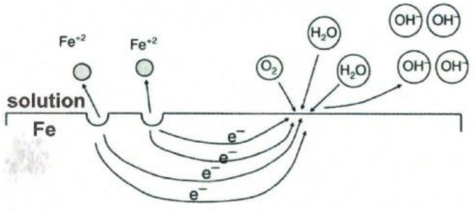
- **Uniform corrosion is the thinning of metal evenly over the whole metal surface area, with no localized attack**
- **Example: Iron (Fe) corrodes faster than any other engineering material in marine and industrial environments**
- **The metal surface is covered with many anodic and cathodic sites which change polarity as corrosion progresses**



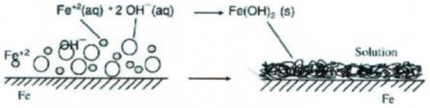
Additional Slides: Uniform Corrosion

- **Corrosion of metals in the natural outdoor atmosphere occurs above a critical level of humidity; this is typically 50 – 70% for most metals, of the order of 60% for iron.**

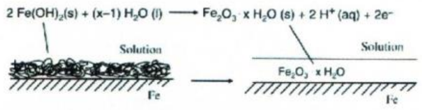
a) Coupled electrochemical reactions occurring at different sites on iron surface in neutral solution



b) Precipitation of ferrous hydroxide



c) Conversion to hydrated ferric oxide



Module 7
(section a)

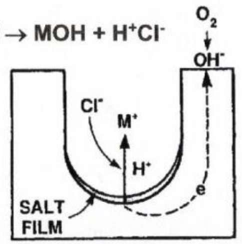
Additional Slides: Pitting Corrosion

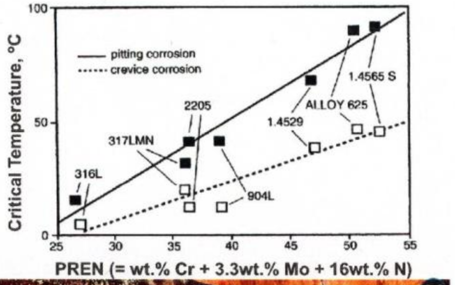
Pitting is a form of localized corrosion where a very small area corrodes preferentially leading to cavities and pits – the bulk of the surface remains unattacked

Metals which form protective passive layers such as aluminium, stainless steels and copper alloys are most susceptible

Metrics associated with pitting resistance include PREN, CPT and critical pitting potential E_p

$M^+Cl^- + H_2O \rightarrow MOH + H^+Cl^-$

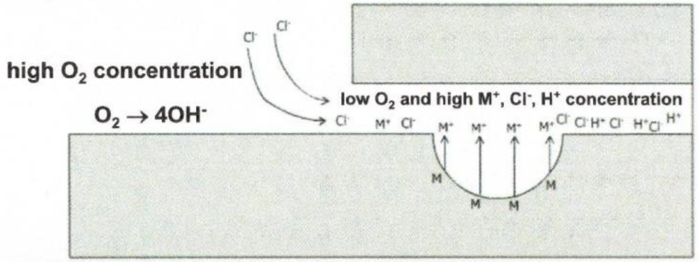




Module 7
(section a)

Additional Slides: Crevice Corrosion

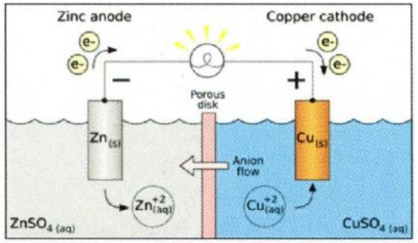
- Crevice corrosion is a localized form of corrosion caused by the formation of a differential aeration cell, exacerbated by deposition of dirt, dust, mud and the existence of voids, gaps, cavities etc.
- Factors influencing crevice corrosion include, crevice type, alloy composition, passive film characteristics, bulk composition of media, mass transfer in and out of crevice

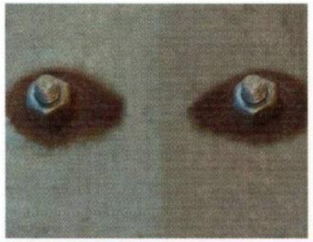


Module 7
(section a)

Additional Slides: Galvanic Corrosion

- See galvanic seawater series – last slides in section
- Galvanic corrosion occurs when two metals with different electrochemical potentials are in metal-to-metal contact in an electrolyte
- Factors affecting degree of attack: position of metals in the galvanic series, anode : cathode area ratio, nature of the environment, distance from junction, geometry





Module 7
(section a)

Additional Slides: Galvanic Corrosion

- Occurs when dissimilar metals are in contact and an electrolyte such as water or other liquid completes the circuit. Avoid by isolating metals from each other.

Also depends on relative surface area

Typical example where fasteners of one metal are used with sheets of another. **Do not use aluminium fasteners with stainless steel sheet**. Stainless steel fasteners with Al sheet OK

Anode (Most Active)

Magnesium
Zinc
Aluminium (2S)
Cadmium
Aluminium (175T)
Steel/Iron
Cast Iron
Lead-Tin Solder
Lead
Nickel
Brass
Copper
Bronze
Stainless Steel (304)
Monel
Stainless Steel (316)
Silver
Graphite
Gold

Cathode (Least Active)

Module 7
(section a)

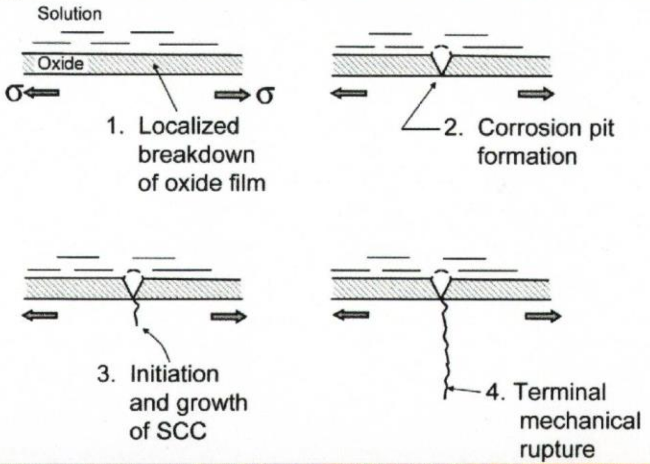
Additional Slides: Stress Corrosion Cracking

- **Stress corrosion cracking arises as a consequence of:**
  - **A product or component being subjected to tensile stress as a consequence of an applied external load, presence of internal residual stress via a fabrication process i.e. bending, welding etc.**
  - **The operating environment is aggressive i.e. high concentrations of ions or other species such as Cl^- (or other halogens), H_2S**
  - **Higher temperatures, typically above 50°C for stainless steels**
- **The result of SCC is frequently sudden cracking and failure of the product without deformation**

Module 7
(section a)

Additional Slides: Stress Corrosion Cracking

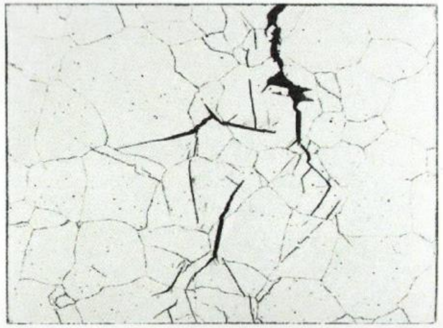
- **Stages in the initiation of stress-corrosion cracks**



Module 7
(section a)

Additional Slides: Stress Corrosion Cracking

- **Transgranular cracks in austenitic stainless (chloride environment)**

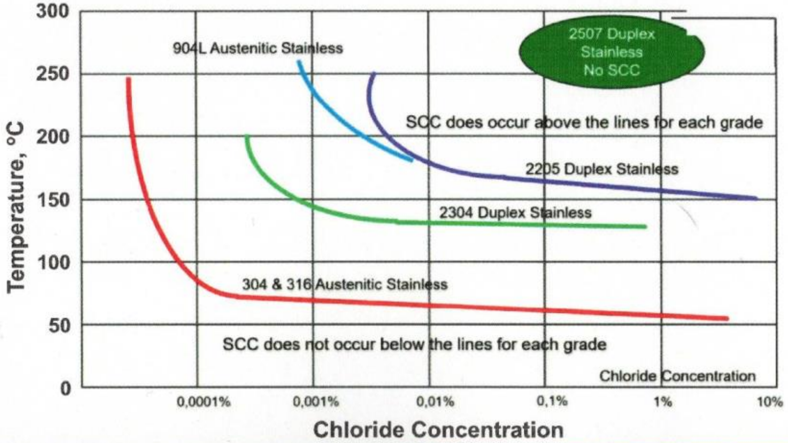


- **Intergranular cracks in ferritic stainless (high temp. caustic environment)**

Module 7
(section a)

Additional Slides: Stress Corrosion Cracking

- **Stainless steel SCC thresholds**



Stress Corrosion Cracking Environments

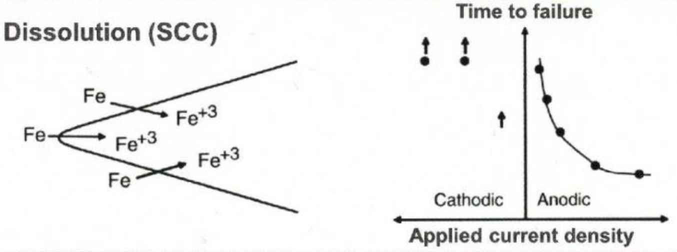
Alloy Types	Environment
High Strength Steels	Seawater Chloride Solutions H2S containing Solutions NO_3^- Solutions
Stainless Steels	Cl^-, Br^-, F^- Solutions Hydroxide Solutions
Aluminium Alloys	Chloride Solutions Most Acqueous Solutions Organic Liquids
Titanium Alloys	Seawater Cl^-, Br^-, F^- Solutions Carbon tetrachloride , other organic solvents including alcohols
Brass (Cu-Zn)	Ammonia solutions, amines, Citrate and tartrate solutions

Hydrogen Embrittlement

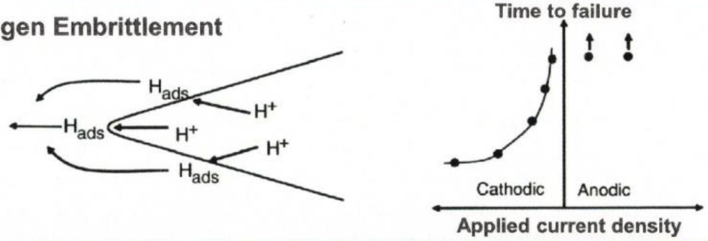
- Hydrogen embrittlement refers to the loss of ductility and cracking that occurs in a metal as a result of hydrogen atoms entering the metal lattice/crystal
- Hydrogen is the culprit because it is a very small atom and is soluble in most metals and hydrogen can be present at a metal surface due to many different sources i.e. corrosion reactions, cleaning in acid solutions (pickling) or from electroplating solutions etc.
- Several proposed mechanisms for hydrogen embrittlement including
  - Build up of internal pressure at voids and flaws due to release of interstitial hydrogen as molecular hydrogen gas
  - Formation of brittle metal hydrides at the crack tip, fracturing of these hydrides allowing further crack propagation
  - Hydrogen aids plastic deformation in advance of a crack

Hydrogen Embrittlement and Comparison with SCC

Anodic Dissolution (SCC)

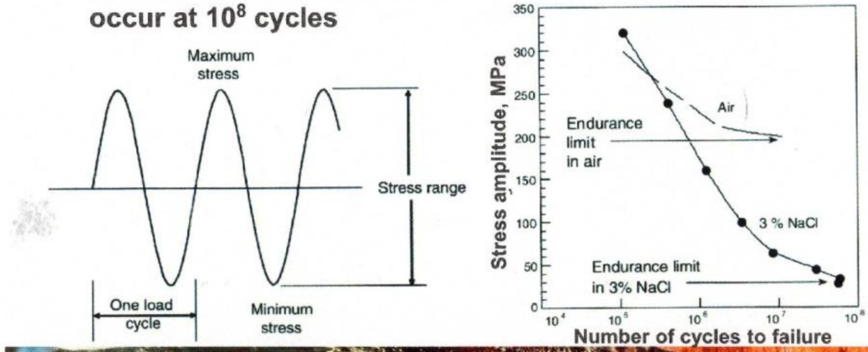


Hydrogen Embrittlement



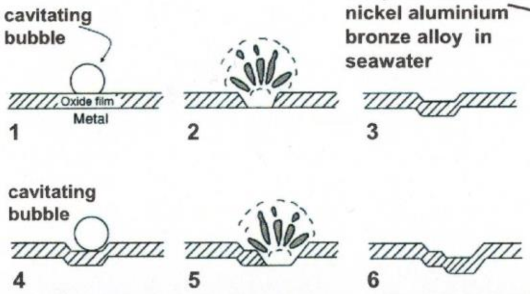
Additional Slides: Corrosion Fatigue

- Environmental cracking under a cyclic load is referred to as corrosion fatigue
- Since no endurance limit is is observed in seawater environments, the corrosion fatigue strength (CFS) is defined as the maximum stress at which failure will not occur at 10^8 cycles

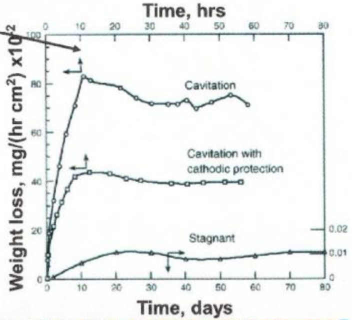


Additional Slides: Cavitation Corrosion

- **Cavitation corrosion/erosion occurs when flow of a corrosive liquid produces a localized pressure differential which leads to bubble formation. The force of collapsing bubbles causes mechanical damage on the metal surface, intensified by the corrosive media**

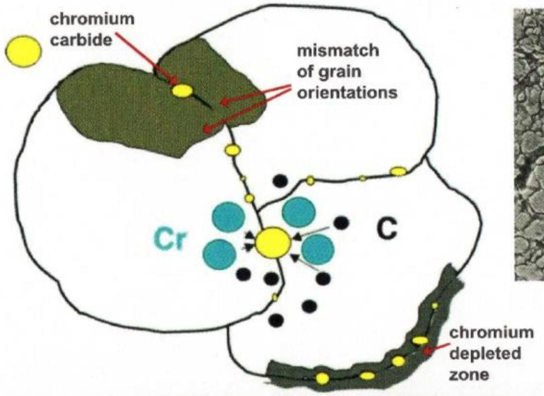


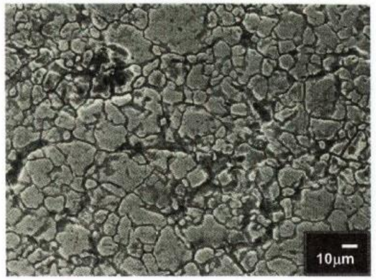
weight loss data for nickel aluminium bronze alloy in seawater



Sensitization in ST/ST and Intergranular Corrosion

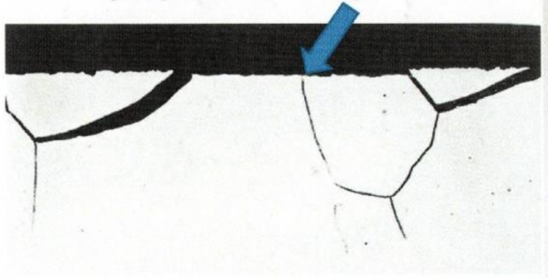
- **Exposure to high temperature (480-900°C) for prolonged duration during welding can promote formation of chromium carbide ($Cr_{23}C_6$) at grain boundaries leaving the material susceptible to IC**

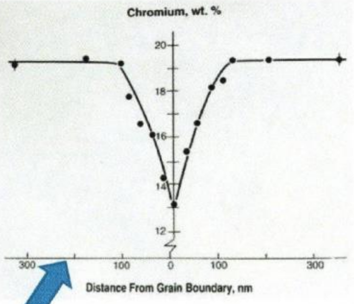




Sensitization and Intergranular Corrosion

- Intergranular attack in a sensitized austenitic alloy produced by exposure to boiling sulfuric-acid - ferric sulfate solution

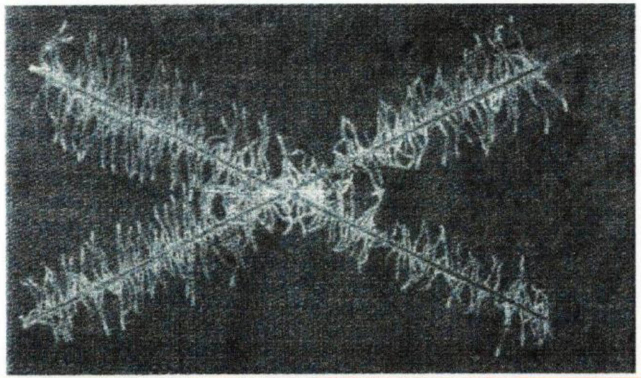




- Chromium concentration profile across a grain boundary between $M_{23}C_6$ carbides in type 304 stainless steel (treated for 10hr at 700°C)

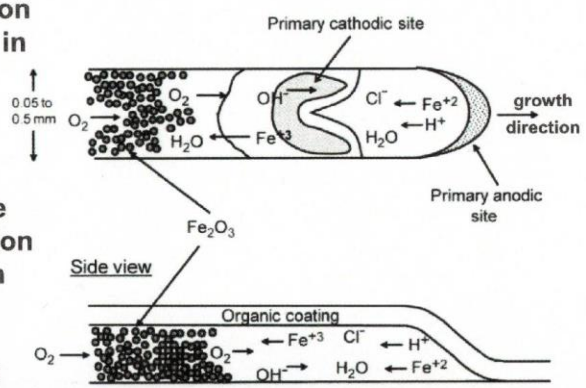
Filliform Corrosion

- **Filliform corrosion is a form of corrosion that occurs under organic coatings in the form of numerous narrow interconnected thread-like filaments. It is observed under organic coatings on aluminium, steel and galvanized steel**



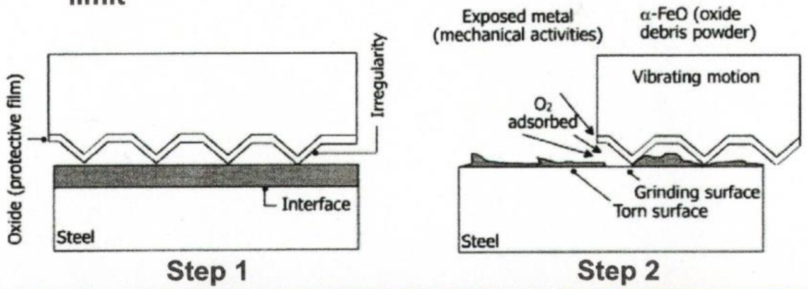
Filliform Corrosion

- Filliform corrosion usually occurs under conditions of high relative humidity and can be considered a special type of atmospheric corrosion.
- This form of corrosion inititiates at a break in a coating where soluble ionic species are present
- Filaments propagate by differential aeration cell in which oxygen enters the filament through its tail and diffuses to the head



Fretting Corrosion

- Fretting corrosion proceeds in three stages
  - Two metallic surfaces are in close contact with reciprocating motion; fretting can be caused by very small movements, s little as 10^{-8} cm
  - The second stage involves oxidation and debris collection
  - Initiation of cracks at low stresses, below the fatigue limit

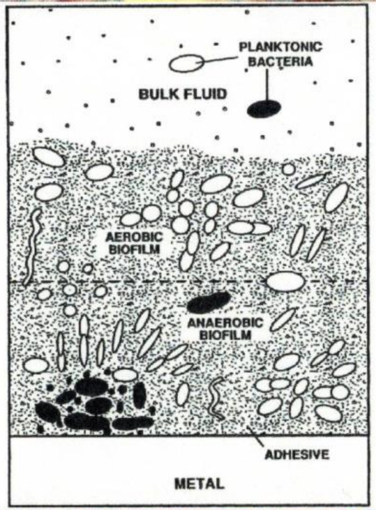


Step 1

Step 2

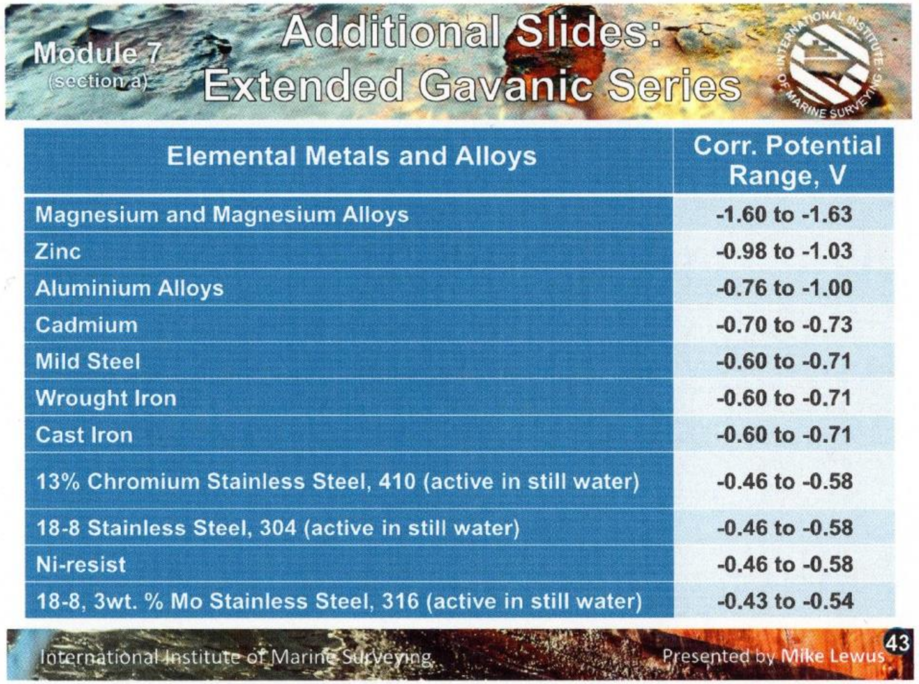
Microbial Induced Corrosion (MIC)

- Microbial slime layers or ‘biofilms’ form over a period of days on all metal surfaces when exposed to acqueous environments containing microbes
- Depending on the consortia this can trigger pitting, crevice corrosion due to ‘potential ennablement’ in stainless steels.
- There are few biocidal metals (copper and its alloys, silver and, to a lesser extent zinc and molybdenum)
- 6% Molybdenum austenitic and 25wt. % Chromium super duplex st/st are more MIC resistant.
- Biofouling more prevalent in warm conditions and in low velocity ($<1ms^{-1}$) seawater



Fretting Resistance of Metal Couples

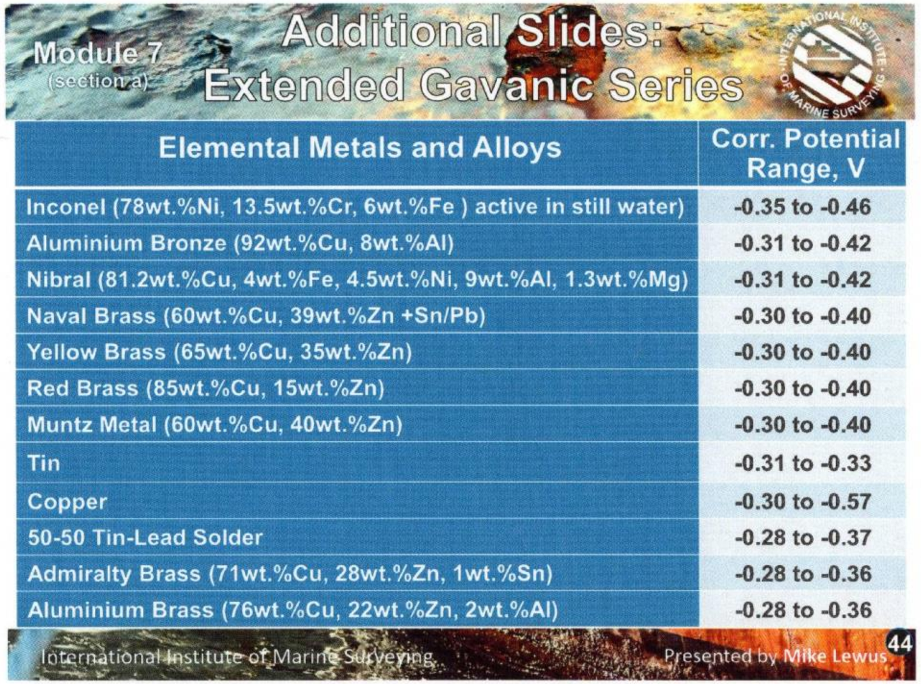
Good	Average	Poor
Cast Iron/Cast Iron + rubber cement coating	Brass/Cast Iron	Aluminium/Cast Iron
Cast Iron/Cast Iron + MoS_2	Cast Iron/Copper Plate	Aluminium/Stainless steel
Cast Iron/Cast Iron + Posphate Conversion coating	Cast Iron/Cast Iron	Cast Iron/Chromium Plate
Cast Iron/Cast Iron + rubber gasketCast	Cast Iron/Silver Plating	Cast Iron/Tin Plating
Cast Iron/Cast Iron + WS_2	Copper/Cast Iron	Magnesium/Cast Iron
Cast Iron/Stainless Steel + MoS_2	Magnesium/Copper Plating	Chromium Plating/ Chromium Plating
Cold Rolled Steel/Cold Rolled Steel	Zinc/Cast Iron	Tool Steel/Stainless Steel
Hard Tool Steel/Hard Tool Steel	Zirconium/Cast Iron	Laminated Plastic/Cast Iron



Module 7
(section a)

Additional Slides: Extended Gavanic Series

Elemental Metals and Alloys	Corr. Potential Range, V
Magnesium and Magnesium Alloys	-1.60 to -1.63
Zinc	-0.98 to -1.03
Aluminium Alloys	-0.76 to -1.00
Cadmium	-0.70 to -0.73
Mild Steel	-0.60 to -0.71
Wrought Iron	-0.60 to -0.71
Cast Iron	-0.60 to -0.71
13% Chromium Stainless Steel, 410 (active in still water)	-0.46 to -0.58
18-8 Stainless Steel, 304 (active in still water)	-0.46 to -0.58
Ni-resist	-0.46 to -0.58
18-8, 3wt. % Mo Stainless Steel, 316 (active in still water)	-0.43 to -0.54



Module 7
(section a)

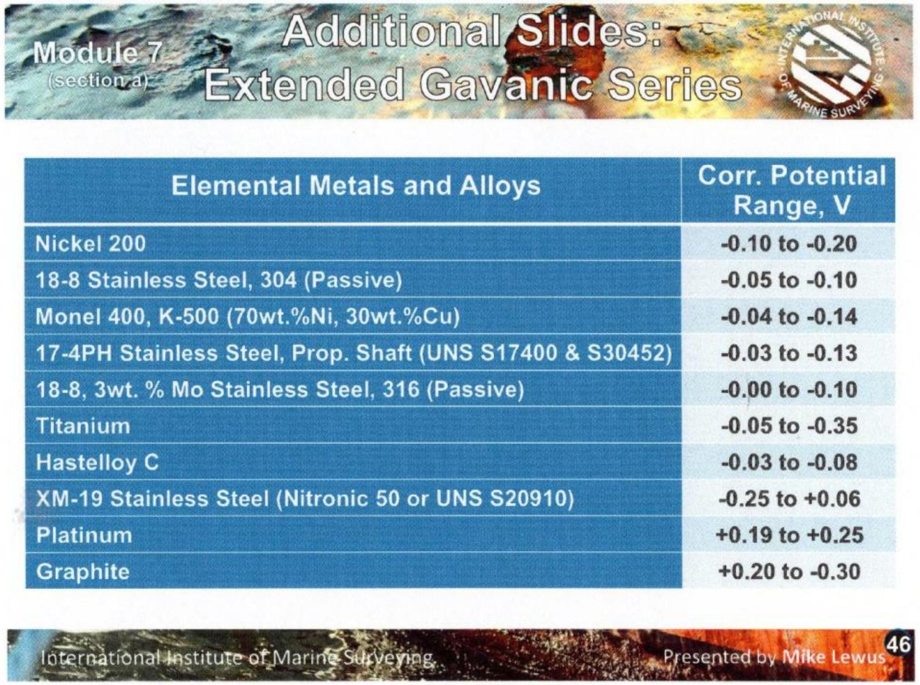
Additional Slides: Extended Gavanic Series

Elemental Metals and Alloys	Corr. Potential Range, V
Inconel (78wt.%Ni, 13.5wt.%Cr, 6wt.%Fe) active in still water)	-0.35 to -0.46
Aluminium Bronze (92wt.%Cu, 8wt.%Al)	-0.31 to -0.42
Nibral (81.2wt.%Cu, 4wt.%Fe, 4.5wt.%Ni, 9wt.%Al, 1.3wt.%Mg)	-0.31 to -0.42
Naval Brass (60wt.%Cu, 39wt.%Zn +Sn/Pb)	-0.30 to -0.40
Yellow Brass (65wt.%Cu, 35wt.%Zn)	-0.30 to -0.40
Red Brass (85wt.%Cu, 15wt.%Zn)	-0.30 to -0.40
Muntz Metal (60wt.%Cu, 40wt.%Zn)	-0.30 to -0.40
Tin	-0.31 to -0.33
Copper	-0.30 to -0.57
50-50 Tin-Lead Solder	-0.28 to -0.37
Admiralty Brass (71wt.%Cu, 28wt.%Zn, 1wt.%Sn)	-0.28 to -0.36
Aluminium Brass (76wt.%Cu, 22wt.%Zn, 2wt.%Al)	-0.28 to -0.36

Module 7
(section a)

Additional Slides: Extended Gavanic Series

Elemental Metals and Alloys	Corr. Potential Range, V
Manganese Bronze	-0.27 to -0.34
Silicon Bronze	-0.26 to -0.29
Bronze – Composition G	-0.24 to -0.31
Bronze ASTM B62	-0.24 to -0.31
Bronze – Composition M	-0.24 to -0.31
13wt.%Cr Stainless Steel, 401 (Passive)	-0.26 to -0.35
Copper-Nickel (90wt.%Cu, 10wt.%Ni)	-0.21 to -0.28
Copper-Nickel (75wt.%Cu, 20wt.%Ni, 5wt.% Zn)	-0.19 to -0.25
Lead	-0.19 to -0.25
Copper-Nickel (70wt.%Cu, 30wt.%Ni)	-0.18 to -0.23
Inconel (78wt.%Ni, 13.5wt.%Cr, 6wt.%Fe) Passive	-0.14 to -0.17



Module 7
(section a)

Additional Slides: Extended Gavanic Series

Elemental Metals and Alloys	Corr. Potential Range, V
Nickel 200	-0.10 to -0.20
18-8 Stainless Steel, 304 (Passive)	-0.05 to -0.10
Monel 400, K-500 (70wt.%Ni, 30wt.%Cu)	-0.04 to -0.14
17-4PH Stainless Steel, Prop. Shaft (UNS S17400 & S30452)	-0.03 to -0.13
18-8, 3wt. % Mo Stainless Steel, 316 (Passive)	-0.00 to -0.10
Titanium	-0.05 to -0.35
Hastelloy C	-0.03 to -0.08
XM-19 Stainless Steel (Nitronic 50 or UNS S20910)	-0.25 to +0.06
Platinum	+0.19 to +0.25
Graphite	+0.20 to -0.30

Professional Qualification
in Marine Corrosion

Presented by **Mike Lewus**

Module 8

(section b)

Corrosion in Ferrous Alloys

Module 8
(section b)

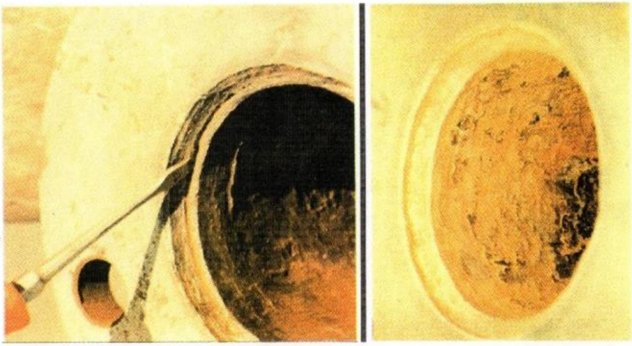
Summary

- **Ferrous Alloys**
  - **Low carbon mild steels**
    - **Plain**
    - **Galvanized**
    - **Polymer coated**
  - **Cast Iron**
    - **Grey cast iron**
  - **Stainless steels**
    - **Austenitic**
    - **Duplex**
    - **pH**
    - **Ferritic**
- **Other Aspects of Corrosion**
  - **PREN, Pitting, Fatigue and prevention**

Module 8
(section b)

Mild Steel: Seawater Piping System (1)

- **Corrosion in flange joint of mild steel seawater piping system**
  - **Leakage at mild steel flanges connected to bronze valves - after 3.5 months service**



Weld metal wasted at screwdriver position and pipe wall thinned by galvanic corrosion – flange directly connected to bronze valve

Flange end 2m away from valve – much lower corrosion level

Mild Steel: Seawater Piping System (2)

- **Cause of seawater pipe damage:**
  - **Corrosion caused by galvanic activity between the mild steel pipe and a bronze valve. LHS figure shows severe metal loss and complete wastage of weld metal in the flange directly connected to the valve. RHS figure shows the flange at the opposite pipe end, 2m away from valve**
- **Remedial Measures:**
  - **Use compatible materials throughout the system or use coated or lined bronze valves. Use of an insulating material to break current flow may be beneficial**
- **Comments:**
  - **Mild steel still likely to corrode, though uniformly making it an unattractive material for seawater piping**

Prevention of Galvanic Corrosion

- **Recommended steps to avoid Galvanic corrosion**

Avoid situations with dissimilar metals in contact with each other

If dissimilar metals are in contact, ensure that ....
- ... the anode has a much larger surface area than the cathode

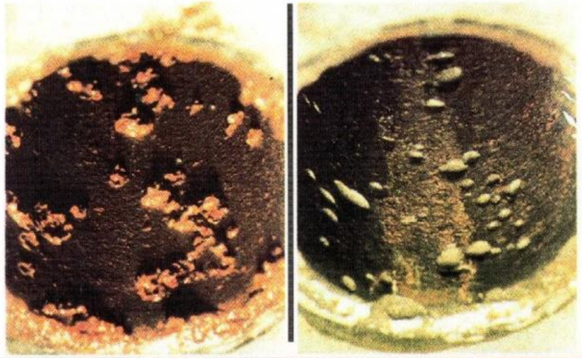
When using dissimilar metals involving fasteners, then ....
- Use stainless steel fasteners for aluminium products
- Never use aluminium fasteners for stainless steel products
- Use stainless steel fasteners for carbon steel products
- Never use carbon steel fasteners for stainless steel products

- **Note that Galvanised carbon steel will suffer corrosion**
  - **If the galvanised layer is damaged or does not cover 100% of the carbon steel – what to do with cut edges?**
  - **Once the zinc is spent corrosion of the carbon steel will accelerate**

    &
  - **Zinc will end up in an aquifer which introduces a toxicity issue**

Galvanized Steel: Seawater Ship Cooling System (1)

- **Localised corrosion on interior of galvanized steel pipe of seawater cooling system on coastal ship**
  - **Local deep corrosion in 3inch diameter cooling water pipe: Conditions - part of time, stagnant seawater at 45°C**



View of pipe interior

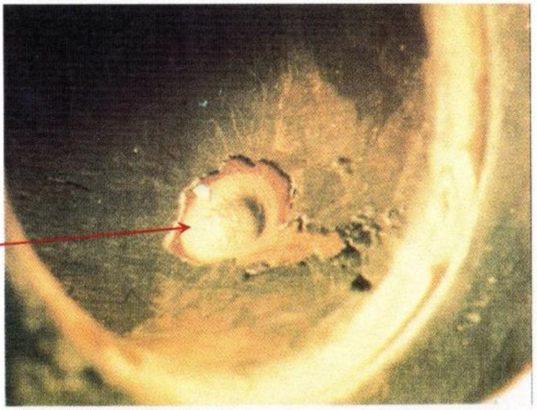
pipe Interior After cleaning

Galvanized Steel: Seawater Ship Cooling System (2)

- **Cause of seawater pipe damage:**
  - **The zinc layer is designed to corrode sacrificially to protect the mild steel substrate, however, it may become passive if exposed to stagnant polluted seawater due to formation of zinc sulphide, thereby preventing sacrificial corrosion.**
- **Remedial Measures:**
  - **Avoid exposure to warm stagnant seawater by draining or maintaining a sufficiently high flow through the system**
- **Comments:**
  - **Copper alloys should not be used as a substitute in these circumstances as sulphide films will promote corrosion**
  - **High molybdenum (>6wt. %) stainless steel (super austenitic), polymer, glass fibre reinforced polyester can give excellent performance**

Epoxy Coated Mild Steel: Seawater Cooling System (1)

- Seawater cooling system on a ship
  - Damage: Serious localized corrosion on pipe wall after 3 months service
  - Piping carried clean seawater



Corrosion attack initiated at site of coating porosity

Epoxy Coated Mild Steel: Seawater Cooling System (2)

- Cause of seawater pipe damage:
  - Corrosion of the pipe wall was caused by ingress of seawater at coating defect site. This is likely to be due to poor substrate preparation and/or poor application of the coating
- Remedial Measures:
  - Clean affected area thoroughly, following adequate surface preparation, repair coating
- Comments:
  - Failure of protective coatings is common, but usually only small areas are affected and repair is possible
  - Serious coating failure usually due to poor preparation of metal surface prior to coating. It is expedient to inspect coatings regularly as breakdown can lead to rapid metal loss – pipe breaches – due to galvanic corrosion

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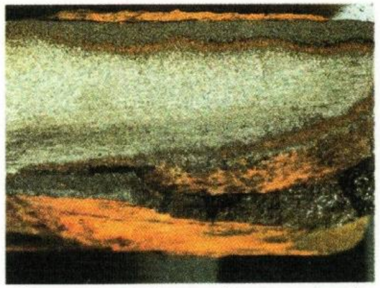
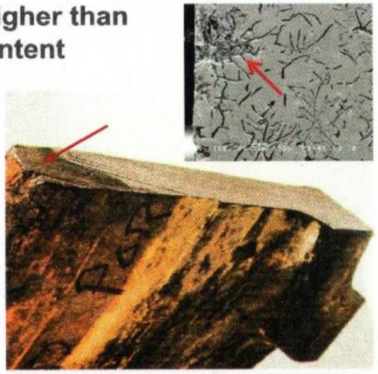
Graphitic Corrosion in Gray Cast Iron (1)

- Pipe joint in cooling water system
  - Damage: Loss of strength due to graphitic corrosion
  - Conditions: Seawater with higher than normal suspended solids content



Cross section of gray cast iron pipe end



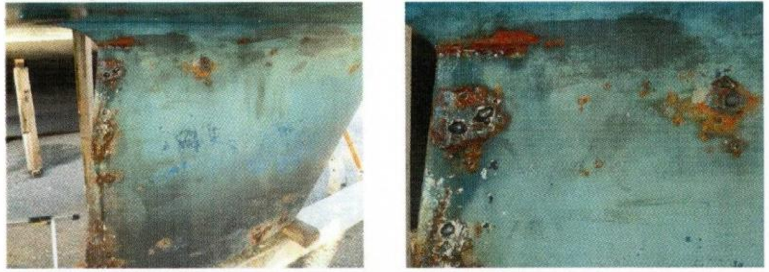
Same section showing more corrosion at the outer surface

Graphitic Corrosion in Gray Cast Iron (2)

- Cause of seawater pipe damage:
  - Enhanced attack taking the form of graphitic corrosion was found at pipe joints of a ‘dresser’ (slip-joint) type coupling i.e. metallic components selectively leached or converted to corrosion product leaving the graphite phase intact
  - The most severe corrosion occurred at the pipe end, within the coupling, caused by slight galvanic effect from the coupling material or the development of low pH in the stagnant area on the external pipe
- Comments:
  - This type of graphitic corrosion is typical of gray cast iron exposed to seawater. Due to heavy wall thicknesses gray cast iron may nevertheless give satisfactory service for many years – in this case for more than 20 years

Corrosion in Gray Cast Iron: Casting Defect

- Corrosion on the keel of a Westerley Fulmar; previous year lift revealed no significant corrosion problems. Parts off the keel had been over painted and this could have covered earlier repair work
- Close view of features showed deep cavities present on one side only, cavities smooth, rounded and grey in colour



- Cause judged to be casting porosity

Crevice Corrosion in 316 Stainless

Crevice Corrosion Example

- View of a port side T-toggle shows relatively uniform surface staining but toggle failed on dismantling
- Threaded stainless steel fittings of this type should be regularly disassembled and inspected for crevice corrosion

Crevice Corrosion in Austenitic Stainless Steel

- Piping system handling water from the Mediterranean sea
  - Damage: Severe corrosion occurred beneath the gasket of all flanges; in service using clean filtered seawater for 16 months
  - Pipes and flanges made from AISI 321 (1.4541)

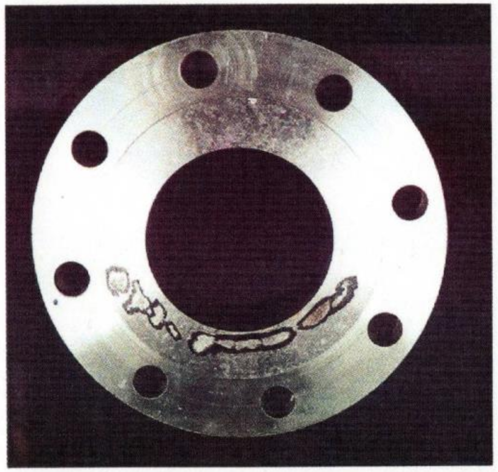
Crevice Corrosion in Austenitic Stainless Steel

- Cause of seawater pipe flange damage:
  - The piping system had been manufactured from a material which is prone to crevice corrosion in seawater i.e. PREN 17-19 – see slides 18, 19
- Remedial Measures:
  - Material selection issue, stainless steels in continuous contact with seawater should have PREN ≥ 40
- Comments:
  - Typically this type of corrosion is alleviated by using compressible gaskets or petrolatum sealants are recommended for offshore environments, including splash zones, refineries, power plants, bridges, buildings, mining equipment and general structural steel

Module 8
(section b)

Crevice Corrosion in Duplex Stainless Steel

- **Piping system carrying seawater**
  - **Leakage occurred at the flanges after approximately 6 months service. Detailed inspection revealed severely attacked flange faces**
  - **Material: Duplex stainless steel UNS S31803 [2205 (1.4462)]**



Module 8
(section b)

Crevice Corrosion in Duplex Stainless Steel

- **Cause of seawater pipe flange damage:**
  - **Crevice Corrsion had occurred within the flanges. This alloy is susceptible to crevice corrosion and as such is unsuitable for use in seawater handling systems i.e. PREN of 2205 is 30.8-38.1 (value ≥ 40 required)**
- **Remedial Measures:**
  - **Use an alternative alloy such as high molybdenum (> 6wt. %) stainless steel or the 90/10 copper-nickel alloy. These alloys are considerably more resistant to crevice corrosion**
- **Comments:**
  - **If the expected water velocity is high the 90/10 copper-nickel alloy may be prone to erosion-corrosion damage. Cathodic protection can alleviate pitting and crevice corrosion damage in 2205 and similar stainless steels**

Module 8
(section b)

Crevice Corrosion in PH17-4 Stainless Steel

Crevice Corrosion in 17-4 Prop. Shaft

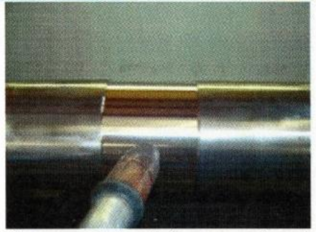
- **The location of the crevice indicates that the propeller has slightly overlapped the taper exacerbating the problem**
- **Having formed the circumferential groove corrosion has continued toward the keyway**
- **The prop. was easily removed suggesting it had not been fully tightened on installation !**

Module 8
(section b)

Erosion Corrosion on Propeller Shaft

- **Erosion-corrosion wear on propeller shaft removed from cutlass bearing**
- **Options: shaft can be replaced or diameter built-up and remachined to specification**

Repair of Prop. Shaft Using Weld Overlay



Repair area cut back & prepped on lathe

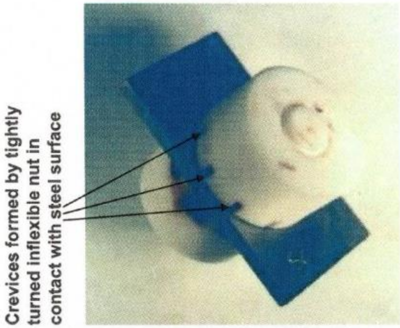
Repair area built back up with weld overlayer

Welding complete

First machining pass back to spec.

Critical Crevice Temperature (CTT) and Testing

- Crevice corrosion resistance follows a similar pattern to pitting resistance but is more severe for the same conditions
- Critical Crevice Temperature (CCT) can be measured by using a test piece with deliberately produced crevices



Crevices formed by tightly turned inflexible nut in contact with steel surface

Grade	Typical CPT, °C	Typical CCT , °C
304 (1.4301)	10	<0
316 (1.4401)	20	<0
2205 (1.4462)	30	20
904L (1.4539)	40	10
Nitronic 50	40	----
Superduplex	65	35
6% Mo	65	35

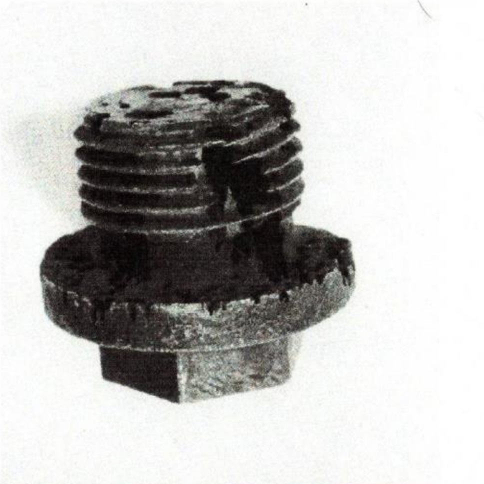
Prevention of Crevice Corrosion

- **Recommended steps to prevent crevice corrosion**

Optimize product / component design	• Design to minimize joints with fixings as far as possible • Use welded parts to eliminate crevices caused by traditional fixing joints • Design products / components for complete drainage
Regularly clean to remove deposits	
Select a suitably corrosion resistant stainless steel	• Appropriate for the operating environment
Use all stainless materials to prevent other corrosion types	

Pitting Corrosion in Ferritic Stainless Steel

- **Plug in seawater piping system**
  - **Pitting attack on plug**
  - **Material: Ferritic stainless steel type 434 (1.4113) in 316L austenitic stainless steel pipe**
  - **Conditions: Seawater at ambient temperature, flow velocity 2ms^{-1}, prolonged stagnation periods**

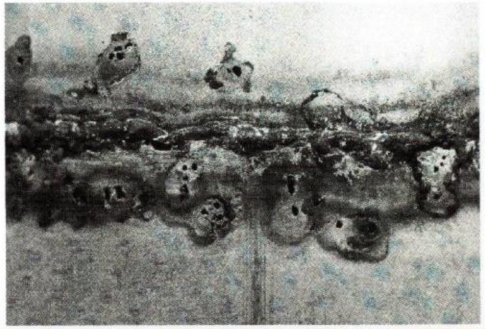


Pitting Corrosion in Ferritic Stainless Steel

- Cause of pipe damage:
  - The type of stainless steel used for the manufacture of the plug is not resistant to corrosion in seawater, the intensity of attack is exacerbated by galvanic activity with the more noble austenitic stainless steel pipework
- Remedial Measures:
  - A plug of material similar in composition or more noble than that of the pipework should be used. However, 316L is not suitable for use in seawater unless it is protected by a cathodic protection system

Pitting Corrosion in Austenitic Stainless Steel

- Austenitic stainless steel piping – seawater fire fighting installation
  - Damage: Leaking pipes due to pitting corrosion along circumferential weld seam
  - Pipes and flanges made from AISI 316L (1.4404)



Pitting Corrosion in Austenitic Stainless Steel

- Cause of pipe damage:
  - Pitting corrosion in weld HAZ. The corrosion resistance of the weld seam is less than that of the base metal especially in the heat affected zone arising in this case from insufficient inert gas cover and/or non removal of oxidized layer
- Remedial Measures:
  - Though 316L (1.4404) may be usable in cold clean seawater service (<10°C), depending on residence time + maintenance/cleaning frequency, it does require the removal of any heat tint affected regions
- Comments:
  - Type 316L stainless steel is not generally recommended for seawater applications. Use the high molybdenum (>6wt. %) stainless steel grades, CuNi alloys or polymers

Pitting Resistance and PREN

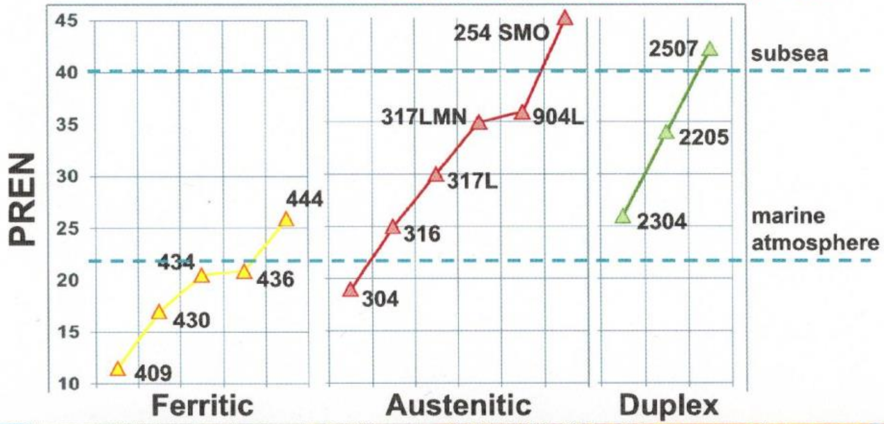
- Pitting resistance equivalent number (PREN) offers a simple method of comparing different grades PREN = Cr + 3.3(Mo + 0.5W) +16N

Grade	Minimum PREN
3CR12 (1.4003)	10.5
430 (1.4016)	16
304 (1.4301)	17.5
316 (1.4401)	23
2205 (1.4462)	31
904L (1.4539)	32
Nitronic 50 (1.3964)	33
Superduplex (1.4410, 1.4501, 1.4507)	40
6% Mo (1.4529, 1.4547)	42

- PREN is a guideline, material selection is more complicated. The Critical Pitting Temperature is a more accurate assessment of pitting resistance

Pitting Resistance and PREN

- Pitting resistance equivalent number (PREN) and corrosion resistance **PREN = Cr + 3.3(Mo + 0.5W) +16N**



Prevention of Pitting Corrosion

- Recommended steps to prevent pitting corrosion

Understand the operating environment
- Environmental corrosive media and contact mechanisms
- Operating conditions …. operating temperature range (min, max, average)

Determine the appropriate PREN required
- Guidance may be found in the appendices

Recognize that the operating environment may change
- Over the lifetime of the installation
- This needs to be factored in when selecting the stainless grade

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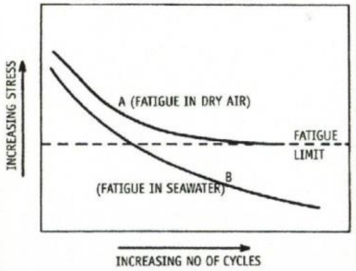
Fatigue in Free Machining 321 Stainless Steel

- Fracture of a 108mm diameter ship seawater/cargo, pump shaft
- Material, free machining 321 stainless steel



Fatigue in Free Machining 321 Stainless Steel

- Cause of shaft damage:
  - The 108mm diameter shaft had fractured due to fatigue originating from several sites in a circumferential groove located between the seals and the main bearing. The fatigue cracks had propagated through approximately 50% of the load bearing cross section before final fracture by ductile shearing. The stresses required for this type of failure or high torsional loading and a misaligned shaft may have contributed to the failure
- Remedial Measures:
  - Inspect the assembly for signs of misalignment and replace the shaft with a stronger alloy that has a corrosion resistance comparable or better than 316 i.e. duplex stainless steel or Monel K500

Module 8
(section b)

Prevention of Fatigue

Grade	min. 0.2% PS, MPa	min. UTS, MPa	Fatigue Limit, Mpa, R=-1	Fatigue to UTS Ratio
1.4301 (304)	210	520	234	0.45
1.4401 (316)	220	520	234	0.45
1.4462 (2205)	460	640	384	0.60

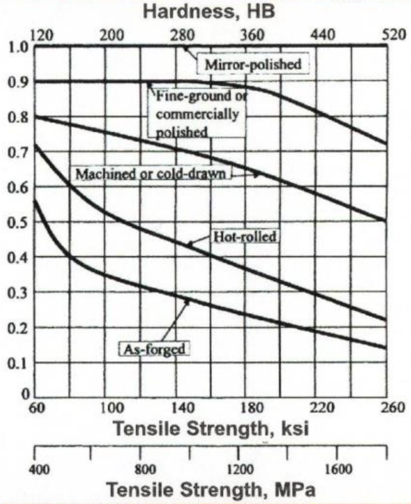
- Fatigue failure is difficult to predict from basic data
- Its occurence depends on specific factors such as product, presence of localised stresses, stress raisers
- If possible test the specific product under conditions replicating service conditions

---

Module 8
(section b)

Prevention of Fatigue

- As most fatigue failures originate at the material surface, surface condition has a significant influence on fatigue
- Figure opposite shows the effect of surface finish on the fatigue limit of steel
- NB the higher the UTS and hardness the greater the reduction of fatigue limits



International
Institute of
Marine
Surveying

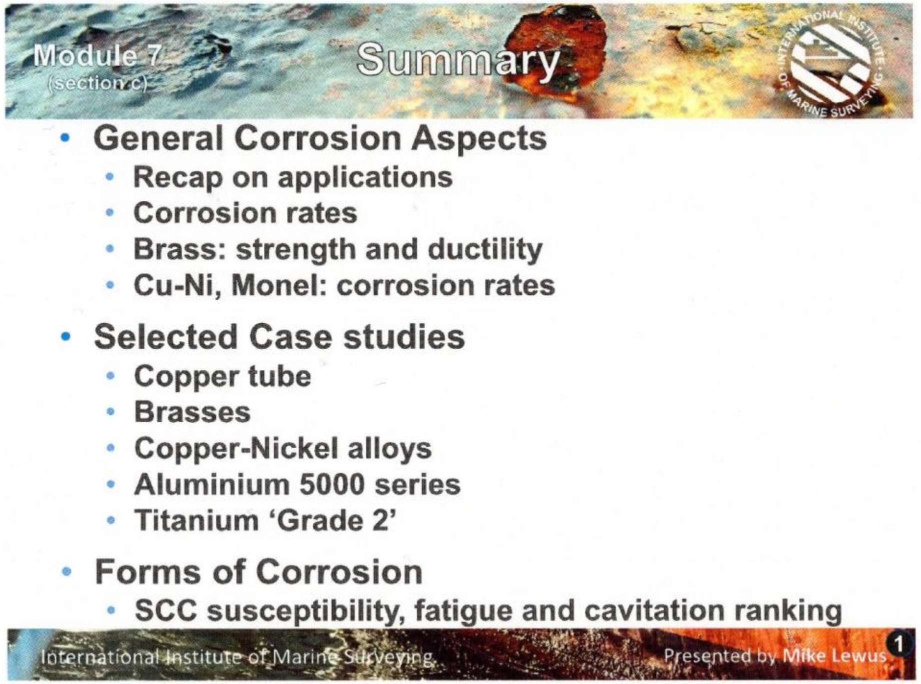
Professional Qualification in Marine Corrosion

Presented by **Mike Lewus**

Module 8

(section c)

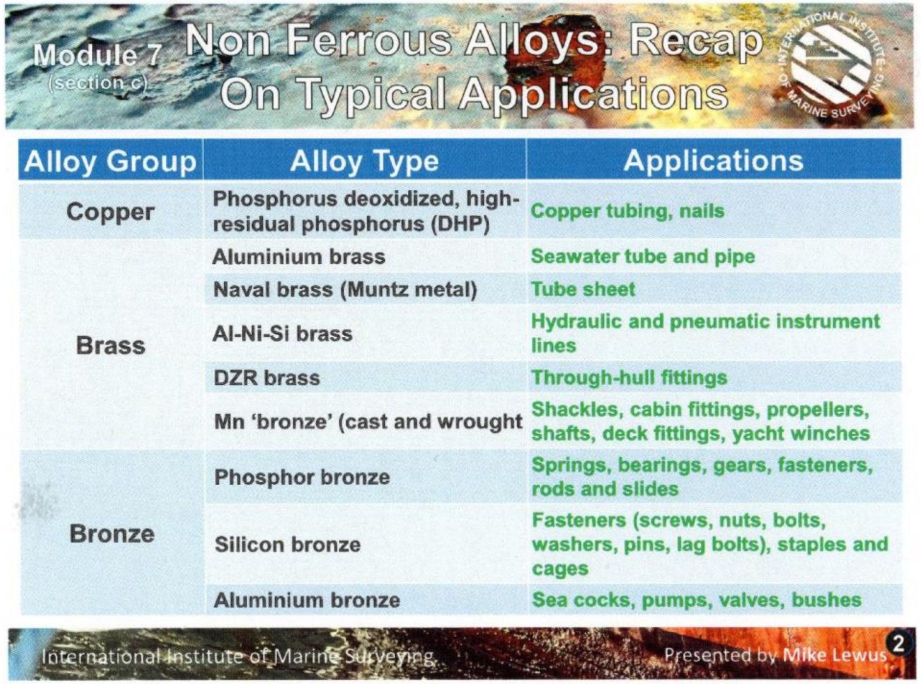
Corrosion in Non-Ferrous Alloys



Module 7
(section c)

Summary

- General Corrosion Aspects
  - Recap on applications
  - Corrosion rates
  - Brass: strength and ductility
  - Cu-Ni, Monel: corrosion rates
- Selected Case studies
  - Copper tube
  - Brasses
  - Copper-Nickel alloys
  - Aluminium 5000 series
  - Titanium 'Grade 2'
- Forms of Corrosion
  - SCC susceptibility, fatigue and cavitation ranking



Module 7
(section c)

Non Ferrous Alloys: Recap On Typical Applications

Alloy Group	Alloy Type	Applications
Copper	Phosphorus deoxidized, high-residual phosphorus (DHP)	Copper tubing, nails
Brass	Aluminium brass	Seawater tube and pipe
	Naval brass (Muntz metal)	Tube sheet
	Al-Ni-Si brass	Hydraulic and pneumatic instrument lines
	DZR brass	Through-hull fittings
	Mn 'bronze' (cast and wrought	Shackles, cabin fittings, propellers, shafts, deck fittings, yacht winches
Bronze	Phosphor bronze	Springs, bearings, gears, fasteners, rods and slides
	Silicon bronze	Fasteners (screws, nuts, bolts, washers, pins, lag bolts), staples and cages
	Aluminium bronze	Sea cocks, pumps, valves, bushes

Non Ferrous Alloys: Recap Typical On Applications

Alloy Group	Alloy Type	Applications
Bronze (continued	Nickel aluminium bronze (cast and wrought)	Propellers and shafts, pumps and valves, bushing and bearings, fasteners and tube plate for titanium tubing in condensers
Gunmetal	Cu-Sn-Zn castings	Pumps and valves, stern tubes, deck fittings, gears and bearings, bollards and fairleads
Copper-Nickel	90/10 and 70/30	Heat exchanger and condenser tubes, platform leg and riser sheathing
	Cu-Ni-Cr	Seawater cast pump and valve components
High-strength Copper-Nickel	Cu-Ni-Al	Shafts, drive bearings, pumps, valves
	Cu-Ni-Sn	Drill components, subsea connectors
Copper-Beryllium	Cu-Be	Drill components, subsea cable housings, hydrophones & geophones, subsea valves and actuator units

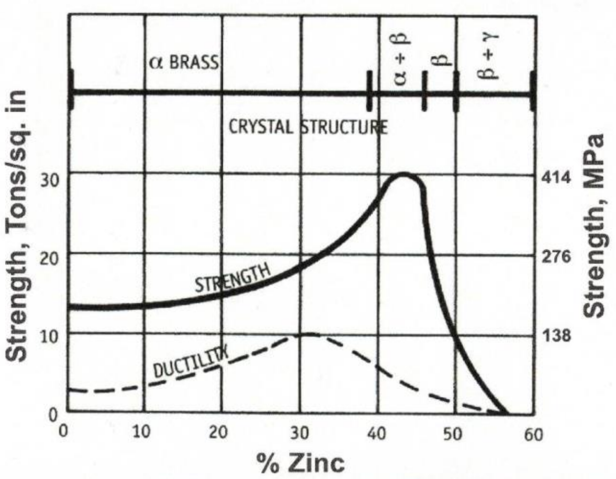
Corrosion Rates for Metals in Quiescent Waters

- Corrosion rates in 'mils', multiply by 25 for value in μm
- Alloys marked '1' are liable to pit
- Alloys marked '2' are liable to dealloy

Metal Alloy	Seawater	Fresh Water
Titanium	0	0
Ni-Cr-Mo Alloys	0	0
316 Stainless Steel	0^1	0
304 Stainless Steel	0^1	0
Copper-Nickel Alloys (Monels)	0^1	0
Nickel-Aluminium Bronze (NAB)	1-2	0
Copper-Nickel Alloys	0.1-0.5	0
Lead	0.5	0.5
Tin Bronzes	1-2	1
Silicon Bronzes	1-2	1
Brasses	$0.5\text{-}2^2$	1
Aluminium Bronze	$1\text{-}2^2$	1
Austenitic Cast Iron	2	1
Steel, Iron	5	2
Aluminium Alloys	1-3	0.1
Zinc	1	0.5

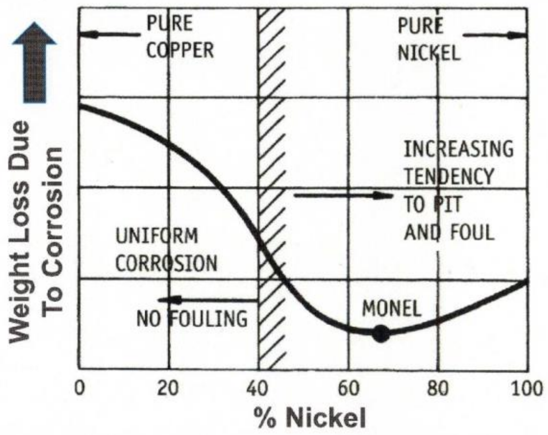
Copper Alloys: 70/30 and 60/40 Brasses

- Two common types of brass are 70/30 (α) and 60/40 (α+β) types
- The 70/30 'alpha' brasses are more ductile, while the 60/40 'alpha-beta' are strongest
- The greater the amount of zinc the more liable the brass to dezincification



Copper Alloys: Monels

- Two common Cu-Ni alloys 'Monels' are Monel alloy a 70/30 Ni/Cu alloy and Monel alloy K500 which has 2-4wt.% of aluminium added and is a stronger alloy
- Monels are very resistant to high water velocities and are often used in water pump parts

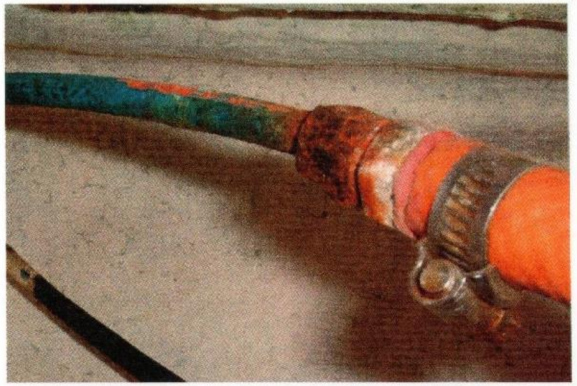


Galvanic Corrosion: Ferrous and Non Ferrous

- **Galvanic corrosion of jubilee clip on gas hose Hose clip found in galley behind cooker hence any leak would feed directly into the accommodation area**

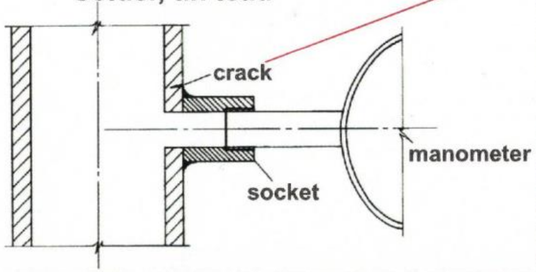
Galvanic Corrosion: Ferrous and Non Ferrous

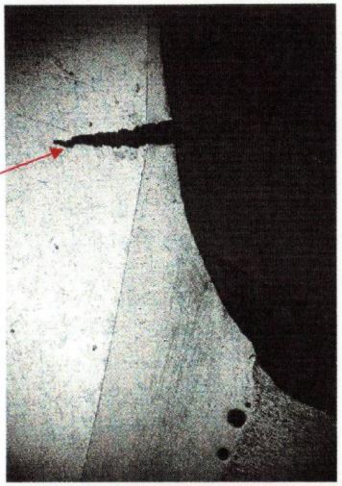
- **Galvanic corrosion in ferrous fitting/copper tubing material couple; a commonly encountered situation. Copper tube is pitted and ferrous fittings badly rusting**



Aluminium Brass: Fatigue Cracking

- **Fatigue cracking in Aluminium Brass (Naval Brass)**
  - **Materials, manometer socket naval brass 61Cu/38Zn/1Sn/0.04As**
  - **Main pipe, aluminium brass 78Cu/20Zn/2Al/0.04As**
  - **Solder, tin-lead**



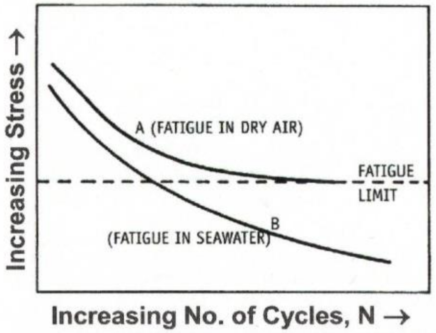


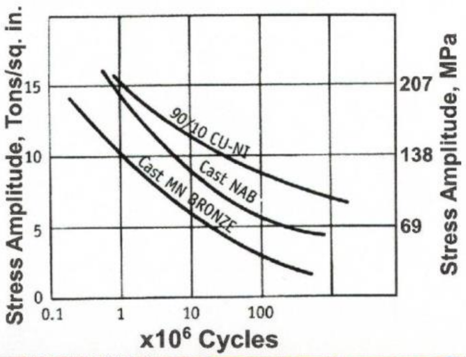
Aluminium Brass: Fatigue Cracking

- **Cause of seawater pipe damage:**
  - **Conditions: Seawater cooling system on a ship**
  - **Conditions: Ambient temperature in machinery room**
  - **The overhanging manometer was excited by structural vibrations (always present on ships). The lead-tin solder has a very low fatigue strength and once a fatigue crack has formed, it propagates through the metallurgical bond into the substrate metal**
- **Remedial Measures:**
  - **More robust support for the manometer and/or use welded-on sockets that have a higher fatigue endurance limit**

Fatigue: Endurance Limit and Effect of Seawater

- In clean air an endurance limit is observed i.e. a stress amplitude below which a metal can endure any number of stress reversals without cracking
- In seawater no endurance limit is observed





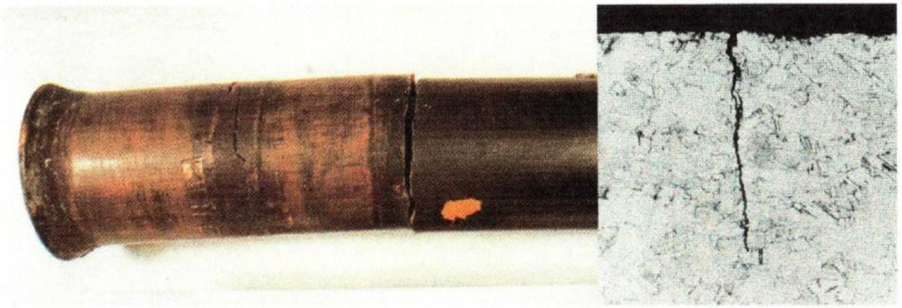
Fatigue Strength of Metals

- Fatigue strength of metals at 100 million cycles in seawater

Alloy	UTS (MPa)	Corrosion Fatigue Strength (MPa)
Mild Steel	412	13.7
Cast Manganese Bronze	500	54.9
Cast Nickel-Aluminium Bronze	598	86.3
Type 316 Stainless Steel	588	137.3
Type 304 Stainless Steel	549	104
Monel K-500	1216	179.5
Hastelloy Alloy C	745	220.7
Inconel Alloy 625	892	276.6

Stress Corrosion Cracking in Admiralty Brass

- Through wall stress corrosion cracking adjacent to roller expanded tube-to-tube plate joints
- Installation: 500MW river water cooled steam condenser in a power station



Stress Corrosion Cracking in Admiralty Brass

- Material and Conditions:
  - Tubes made from Admiralty brass
  - The condenser was cooled by river water flowing at a nominal velocity of $2ms^{-1}$
- Cause of Damage
  - Condenser subject to an unexpected long down time period. The condenser was not adequately drained and stagnant water conditions arose due to decaying organic matter. This in combination with high residual tensile stresses in the tube material caused by the roller expansion process, resulted in SCC
- Remedial Measures
  - Condenser retubed with 90:10 copper-nickel alloy which is resistant to SCC under these conditions

Stress Corrosion Susceptibility of Metals

Susceptible Metals	Environment
Very high strength steels: yield strength > 1400MPa	Seawater, freshwater, on deck
High strength aluminium alloys: yield strength > 400MPa Wrought aluminium alloys with > 3wt. % Mg	Seawater, freshwater, on deck
316 stainless steel 304 stainless steel	Hot seawater >60°C, steam and hot caustic soda
Carbon steel	Hot caustic
Brass with > 15wt.% zinc and manganese bronze	Seawater and ammonia (polluted seawater)
Aluminium brass Aluminium bronze	Ammonia and steam

Stress Corrosion Susceptibility of Metals

Non susceptible metals under normal boating conditions in or out of the water	
Copper	Aluminium alloys
Titanium	Lead
Stainless steel Types 304 and 316	Copper-nickels
Silicon Bronze	Gunmetal
Aluminium Bronze	Aluminium brass
Mild steel and cast iron	
Nickel based alloys e.g. Monel and Ni-Cr	
Nickel-aluminium bronze	
Brass and manganese bronze (on deck)	

Monel Impeller: Impingement Attack

- **Ship seawater circulatory pump found to have significant cavitation erosion damage after 4 years service**

Monel Impeller: Impingement Attack

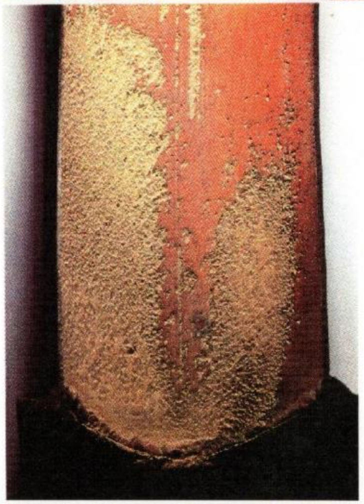
- **Material:**
  - **Pump impeller made from Monel, though analysis revealed it did not meet the relevant specification**
  - **The impeller had been fitted into a high speed centrifugal pump made from a leaded gunmetal**
- **Nature of Damage**
  - **Leading edge of the suction sides of the impeller blades exhibited severe metal wastage that could be attributed to cavitation erosion. The damage became apparent after 4 years service**
- **Cause of Damage**
  - **A detailed examination showed that the impeller was very porous and cracking was evident. The material had been subjected to a form of selective denickelification.**

Monel Impeller: Impingement Attack

- **Cause of Damage**
  - **The denickelification was thought to be associated with a poor quality of casting and conditions that occur in pumps when they are not in use and are in contact with stagnant seawater**
  - **The metal wastage at the leading edges of the suction sides of the impeller blades is attributed to cavitation, however, the absence of work hardening in the eroded areas indicates that the cavitation intensity was low**
- **Remedial Measures**
  - **Use more cavitation resistant materials i.e. high performance stainless steel**
  - **Nonmetallic materials such as filled phenolic resins and nylons could also be considered**

Copper – Nickel Alloys: Erosion Corrosion

- **Seawater cooling system**
- **Excessive wall thinning in a copper-nickel pipe, downstream of a branched section of piping**
- **Cause of damage: The average design flow velocity may have been adequate for the specification, but the more aggressive/turbulent conditions produced by an abrupt change in flow direction caused the erosion corrosion**



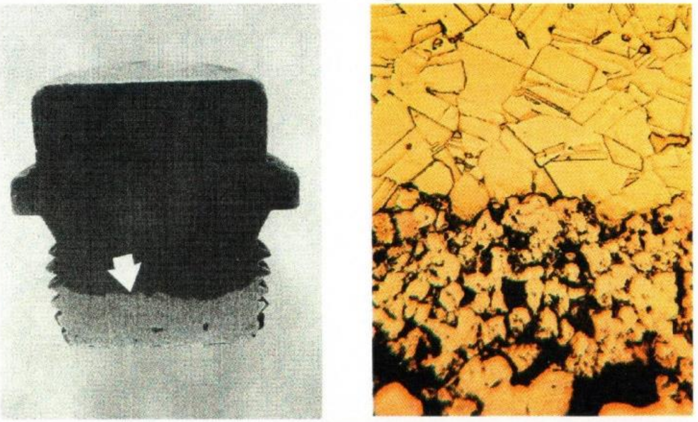
General Resistance to Cavitation: Metal Ranking

- **In general, resistance to cavitation increases with increasing surface hardness**
- **Cathodic protection can be successful in stopping cavitation**
- **Propeller/Impeller design can be used to reduce risk**

Metal Alloy	Cavitation Rating
Titanium	Best
Stainless Steel	
Nickel-Chromium Alloys	
Monel	Good
Nickel-Aluminium bronze	
Gunmetal	Limited Resistance
Manganese 'bronze'	
Copper-nickel alloys	
Cast Steel	Poor
Cast Iron	
Wrought Iron	
Aluminium	

Dezincification in α-β Brass

Seawater piping system: Plug alpha-beta brass, pipes CuNi-10Fe, conditions: flowing seawater at 1.5ns^{-1}

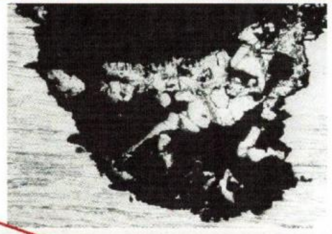


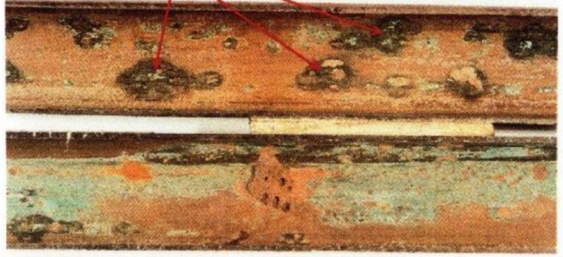
Dezincification in α-β Brass

- **Nature of Damage:**
  - **Dezincification of deaeration plug**
    Plug Material: alpha-beta brass
    Pipework material: CuNi-10Fe
- **Comment:**
  - **Copper base alloys are prone to rapid erosion-corrosion if flow velocities for the alloy are exceeded. The dezincification is possibly aided by galvanic activity between plug and piping**
- **Remedial Action**
  - **Plugs to be made of same alloy as piping**

Material Selection: Keel Bolt Example

- **Localised pitting in Copper-Nickel tubes of a seawater cooled 'dump steam' condenser in a power station**
- **Tubes were made from 66Cu-30Ni-2Fe-2Mn**
- **The condenser was cooled by seawater flowing at a nominal velocity of $2ms^{-1}$**





General Pitting Behaviour of Metals

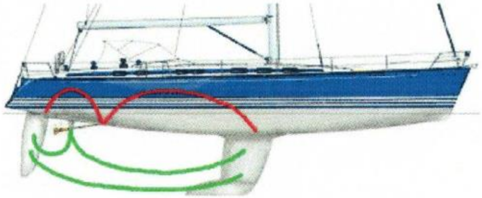
- **Cause of Damage:**
  - **This relatively small condenser was used during commissioning trials at the power station, before the main condensers were available**
  - **Often the incoming steam temperature was 110ºC and it was suspected that the coling water flow rate was less than for the specified design. This combination led to rapid perforation, after only 500hrs on some of the outermost tubes from the cooling side by hot spot corrosion (see tube figure, previous slide)**
- **Remedial Measures**
  - **Condenser was retubed with titanium**
- **Comment**
  - **Copper-nickel alloys are particularly prone to hot spot corrosion and should not be used where this risk is high**

Galvanic Corrosion of 5000 Series Al-My Alloy

- **Galvanic corrosion of aluminium stern drive coupled to stainless steel propeller**

Aluminium Alloys in Marine Applications

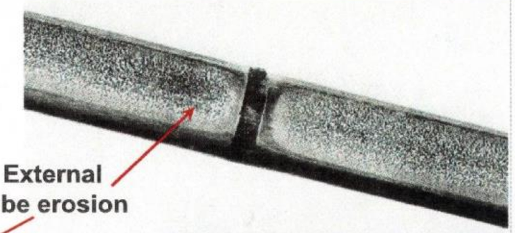
- Consider a yacht with an aluminium rudder shaft, standard propeller drive system and a cast iron keel
- Some boat builders choose to connect all three parts with a copper wire (red line) with the aim of protecting the whole system with a zinc anode

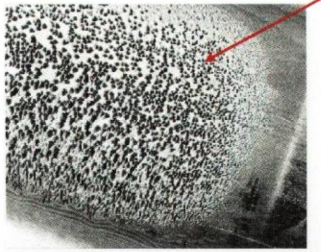


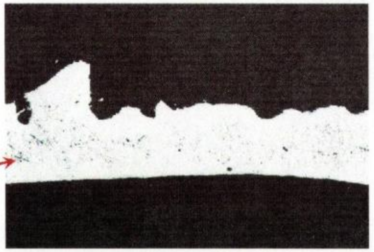
- Problems arise when the zinc anode is either completely spent or, falls off
- The new anode will be the aluminium rudder shaft which will undergo anodic dissolution
- The problem is exacerbated by conditions; greater salinity and warm temperature increases the electrode potential difference, increasing the rate of reaction and hence corrosion rate

Titanium Grade 2: Erosion Corrosion

External Pitting Erosion in titanium tubes of a seawater cooled steam condenser in a power station







Titanium Grade 2: Erosion Corrosion

- Nature of Damage:
  - External pitting erosion. The titanium tubes affected were those adjacent to the steam inlet ducts. Approximately 50% of the tube wall thickness had been removed
  - The damage was caused by impingement of water droplets present in the steam onto the titanium tube surface
- Tubes were cooled by seawater flowing at a nominal velocity of 2ms^{-1}
- Remedial Measures
  - Damaged tubes were plugged off
- Comment
  - Damage may be prevented by fitting non-metallic erosion resistant shields locally