Technical Meeting — 1 May 2019

Jim Galanos, Engineering Manager NSW & ACT, Corrosion Control Engineering, gave a presentation on *Corrosion and Mitigation: Truths, Lies, and Everything in Between* to a joint meeting with the IMarEST attended by 59 on 1 May in the Harricks Auditorium at Engineers Australia, Chatswood. This was the third-highest attendance of our 114 meetings at the Chatswood venue since Engineers Australia moved there in June 2006.

Introduction

Jim began his presentation by saying that corrosion is a massive problem in general, but is particularly so in the marine environment as the conditions are conducive to corrosion, and mitigating corrosion in these environments is challenging. The presentation provided a lot of experiences from years in the game to help designers and maintainers of vessels, as well as giving some facts about corrosion and dispelling myths.

Corrosion Basics

There are four essential requirements for a corrosion reaction:

- a cathode: the metal which is protected against corrosion;
- an anode: the metal which corrodes;
- an electrolyte: the conductive environment which sustains the corrosion process; and
- a conductive bond: the electrical bond between metals, but can be internal within the metal

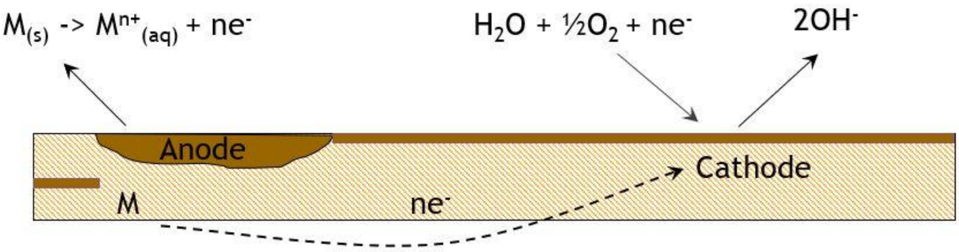
Removal of any of these will stop corrosion.

As a matter of interest, a direct current of 1 amp discharging off steel for a year will cause a loss of steel by corrosion of 9 kg in that year. Oil and gas pipelines typically have wall thicknesses of 6–10 mm, and that rate of corrosion can put a hole in a pipeline in a year.

Structures are now being asked to last longer, often past the original design life and, if there has been loss of metal due to corrosion, then we may have to reduce the operating pressure in a pipeline, or reduce the allowable loads on wharves and jetties, etc.

However, corrosion can be beneficial and the electron flow can be useful: batteries are just corrosion cells, and we rely on batteries for many things. So it is not all bad, just mostly!

In a basic cell, corrosion occurs when a metal "is dissolved" in an aqueous solution. Slight differences in the potential within a metal creates corrosion cells. The anode decomposes into metal ions in solution and electrons. The cathode absorbs the electrons and forms hydroxyl (OH) ions. A potential difference of millivolts will cause corrosion.



Basic corrosion cell
(Diagram courtesy Corrosion Control Engineering)

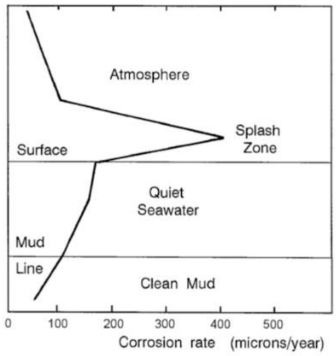
The Hard Truth

The hard truth is that all metals commonly used in the marine industry corrode, with the rate of corrosion depending on the metal and its environment.

- Mild steel immersed in seawater corrodes at an approximate rate of 0.1 mm (100 microns) per year.
- Grade 316 stainless steel immersed in seawater corrodes at an approximate rate of 0.0025 mm (2.5 microns) per year.
- Marine copper alloys (including bronzes) immersed in seawater corrode at an approximate rate of 0.01 mm (10 microns) per year.

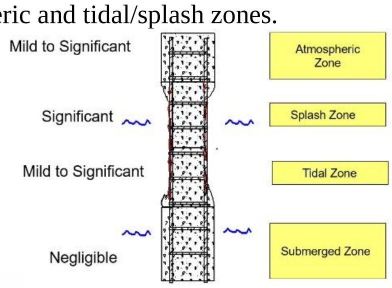
Factors which may influence these rates include temperature, flow rates, microbial activity and oxygen levels. Corrosion rates in tidal and splash zones can be 3–5 times higher. Pitting corrosion and microbial-induced corrosion can be up to several millimetres per year.

The corrosion of steel in seawater depends on the location relative to the water surface, the rate being highest in the splash zone just above the surface.



Corrosion of steel in seawater
(Diagram courtesy Corrosion Control Engineering)

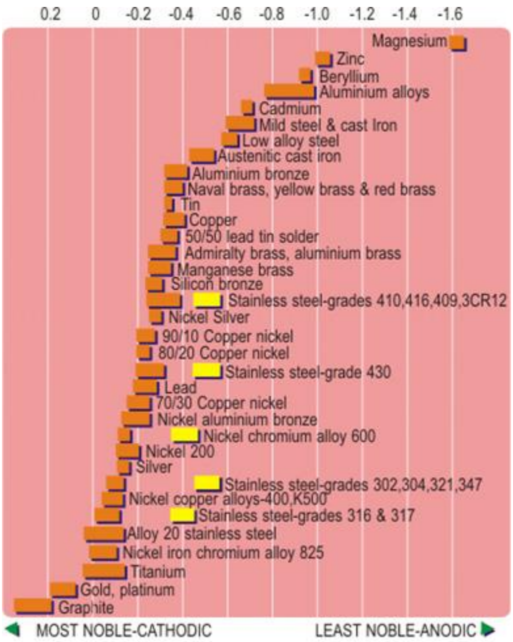
The corrosion of concrete-embedded steel in seawater also depends on the location relative to the water surface, the rate being highest in the atmospheric and tidal/splash zones.



Corrosion of concrete in seawater
(Diagram courtesy Corrosion Control Engineering)

The problem with reinforced concrete in seawater is that the product of the steel corrosion (rust) mostly does not go into solution, but expands (up to 6–8 times the original volume) and cracks the concrete, allowing the access of chlorides which decreases the pH of the concrete and accelerates the whole process.
Pitting corrosion in steel plates can be a real problem. If there is no hole, then the problem is manageable; a hole is not manageable! Some codes and regulations assume uniform corrosion and provide for a corrosion margin on the required thickness of plates; however, it is impossible to design for non-uniform corrosion, i.e. pitting.

The Galvanic Series
Here Jim showed a diagram of the galvanic series and how the electrode potentials of the various metals relate to each other.



The galvanic series (units of volts)
(Diagram courtesy Corrosion Control Engineering)

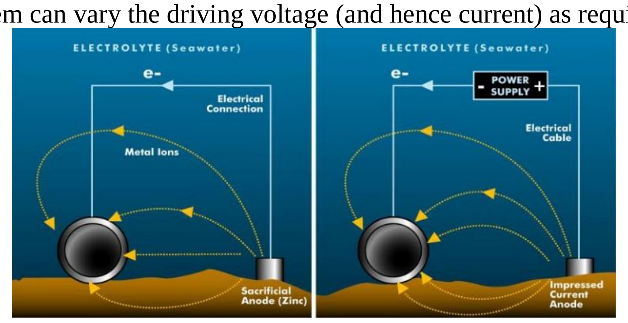
Bonding dissimilar metals increases corrosion rate, and the further apart they are on the galvanic scale, the greater the driving voltage, the higher the current flow between the metals and the higher the rate of corrosion on the more-active metal. What can we do about it?
In Australia, corrosion mitigation is a multi-billion-dollar industry, and it is a multi-trillion-dollar industry in the USA and world-wide. We are interested in arresting corrosion and in extending the service life of structures.

Corrosion Mitigation via Coatings
Coatings are often used as the main corrosion-protection barrier. Coatings provide protection by isolating the metal (usually steel) from the surrounding environment.
The coating manufacturers market their products as perfect and defect free. However, a perfect (100%) coating cannot be applied or maintained. Coating breakdown occurs with day-to-day operation and with age. Having a coating 99% intact means that the coating is not perfect, and corrosion can take place at the 1% which is *not* protected. If the corrosion products expand (e.g. rust), then the affected area becomes larger and the problem becomes bigger.
New epoxy coatings are good, and limit water ingress. However, some of the older coatings, such as coal tar, are now more like sponges!
Coatings are never perfect, and will never be. They break down with age, or damage from impacts, or from abrasion. Given enough time, and this could be many decades, coatings will absorb moisture and will disbond.

Corrosion Mitigation via Cathodic Protection
Cathodic protection is an electrochemical process and involves a direct current being forced to flow from an external source (the anode) to the buried/immersed structure being protected (the cathode). There are two types of cathodic protection:

- Sacrificial anode, typically zinc or aluminium in seawater and brackish environments.
- Impressed current, with a DC power supply; the anode is inert, typically of titanium, platinum or graphite. Titanium and platinum anodes have a metal oxide coating which is the active part of the anode.

Both of these systems do exactly the same thing, although the sacrificial anode has a fixed driving voltage, where the impressed current system can vary the driving voltage (and hence current) as required.



Sacrificial anode and impressed current cathodic protection
(Diagrams courtesy Corrosion Control Engineering)

Cathodic protection (either sacrificial anode or impressed current) is widely used to complement coating systems, with the coating system being the main corrosion barrier. As coatings break down, the cathodic protection system provides protection at coating defects. The formation of calcareous deposits on the surface show that a passive (protective film) is being established, even to previously-corroded steel, and that no more corrosion is taking place.
Note that no *cathodic protection* means *no* protection!

Cathodic Protection of Structures
The following structures *can* be protected from corrosion by cathodic protection:

- Buried, immersed and steel-reinforced concrete structures.
- Berths, wharves, jetties, dolphins, moorings and navigation aids (up to mid tide).
- Sheet piling and driven piles (up to mid tide).
- Structures with existing corrosion (retrofit).

The following structures *cannot* be protected from corrosion by cathodic protection:

- Above-ground structures (this includes land-based vehicles!)
- Above-mid-tide structures.
- Timber structures.

Anyone telling you otherwise is lying!

Wharf piles are often mild steel, can be 30 m long and 1 m diameter, driven into the sea bed and so have buried, water, splash and atmospheric zones to protect. It is expensive to coat the whole length of pipe, so they are often coated down to 1 m below the low-water mark, with cathodic protection underwater and up to the mid-tide mark, so that some areas have double protection.
Internally protecting pipework against corrosion is difficult. Isolating and material selection is the best for pipes.

Interpretation of Corrosion Potentials
The measurement of the potential of a metal (measured relative to a $Cu/CuSO_4$ reference electrode) can be used to indicate its corrosion state in a particular environment. This is detailed in local and overseas standards.
Buried/Immersed Structures

–500 mV	Typical unprotected potential
–850 mV or more negative	Protected against corrosion

Concrete Structures

–200 mV	> 90% Probability of no corrosion
–200 mV to –350 mV	Uncertain corrosion activity
–350 mV or more negative	> 90% Probability of corrosion

Protection Criteria
For buried and immersed structures as per AS2832 Parts1–4

Reference	Protection Potential in Volts	
	Steel	Aluminium
Cu/CuS04	-0.85	-0.95
Ag/AgC1	-0.80	-0.90
Zinc	+0.25	+0.15

*1

Reference	Maximum Potential in Volts
Cu/CuS04	-1.20
Ag/AgC1	-1.15
Zinc	-0.10

Protection criteria according to AS2832 Parts1–4
(Diagram courtesy Corrosion Control Engineering)

Note 1. All potentials are free of significant voltage-gradient error
2. Where MIC/SRB/ALWC [*Microbiologically-influenced corrosion/Sulphate-reducing bacteria/accelerated low-water corrosion*—Ed.] is present, a minimum potential of 100 mV more negative than shown in the table should be maintained

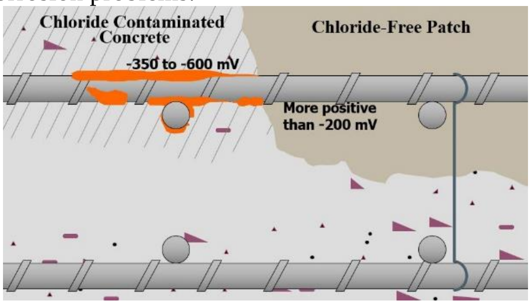
Galvanic (Sacrificial) Cathodic Protection Systems
A sacrificial anode cathodic protection system involves connecting the structure to a sacrificial anode. The anode must be more active (as per the galvanic series) than the metal being protected.
The most common sacrificial anodes are:

Magnesium	Fresh water and non-chloride contaminated soils only and for tank de-scaling
Zinc	Fresh water, salt water and all soil types
Aluminium	Salt water applications and some low-resistivity soil environments

Zinc is limited by temperature, as it passivates at temperatures of about 50°C and higher.
Advantages of sacrificial anode cathodic protection systems include no external power source being required, typically lower supply and installation costs, less maintenance, minimal/no adverse effect on other structure, and minimal/no chance of coating disbondment.
Disadvantages of sacrificial cathodic protection systems include limited driving potential and hence current output, typically shorter design life than impressed current systems, and limited flexibility in controlling output.

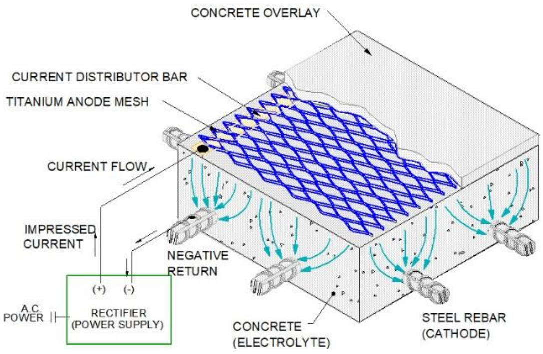
Impressed Current Systems
Impressed current cathodic protection systems involve the use of an external direct-current power supply. The structure is connected to the negative terminal of the power supply whilst the positive terminal is connected to an inert anode (typically mixed-metal-oxide-coated titanium or platinum-coated titanium). Anodes installed in high resistivity ground environments will have a have a calcined coke backfill which increases output and life.
Advantages of impressed current cathodic protection systems include larger driving voltages and hence greater current output, good output control, and typically longer design life than sacrificial anode cathodic protection systems.
Disadvantages of impressed current cathodic protection systems include typically higher supply and installation costs, higher running and maintenance costs, potential to cause adverse effects on other structures, and may cause coating disbonding under certain conditions.

Concrete Patch Repair
Patching concrete can lead to corrosion problems.



Corrosion caused by patching concrete
(Diagram courtesy Corrosion Control Engineering)

In the diagram, the new concrete patch is chloride free, and has a potential more positive than –200 mV. The old concrete is chloride contaminated and has a potential of between –300 and –600 mV. This naturally sets up a galvanic cell, and causes corrosion (rust, coloured orange) on reinforcing steel bars of the old concrete rebar.
One means of obviating this problem is to use a titanium anode mesh with concrete overlay and an impressed current system between the steel reinforcing and the titanium mesh, with the moisture in the concrete as the electrolyte. The same effect can be achieved using ribbon anodes in lieu of mesh. That is, a cathodic protection system is installed to mitigate rebar corrosion.



Concrete overlay titanium mesh system
(Diagram courtesy Corrosion Control Engineering)

Frequently-asked Questions
These new (piles, sheet piling, rebar, etc.) are corroding faster than the existing ones which are 50 years old!
This is not uncommon. Bonding new steel to old steel results in a potential difference in the order of 200–300 mV, with the new steel acting as the anode.
These anodes don't work, the boat's propeller and shaft are still corroding!
You would need to check:

- Whether the anodes are AS2239 compliant; if they are not, then there may be too many or too much impurity which can passivate the anodes which will then not be as efficient as required. In some cases, the anodes will completely passivate and fail.
- Whether all structures are electrically bonded; for example, a propeller-shaft slip-ring assembly ensures good electrical contact between the propeller, propeller shaft and the ship's hull. The assembly comprises a silver-inlaid copper band, clamped to the shaft, and a brush assembly. High silver content brushes running on the silver strip provide electrical continuity.
- Whether there are enough anodes to provide uniform current distribution; distribution of anodes is difficult to teach—it depends very much on experience.

These anodes disbonded my coating.
Sacrificial (zinc or aluminium) anodes in seawater do not have the capacity to shift a structure to over-protected potentials. Coating loss would most likely be due to other factors, such as poor surface preparation and/or application.
However, note that impressed current cathodic protection *can* shift a structure to over-protected potentials and, hence, disbond coatings, for example.

The marina upgraded the on-shore AC power and now my boat is corroding at twice the previous rate.
It is common for marinas and vessels to have insufficient isolation between the marina's electrical earth and adjacent vessels (bonding via the earth). This results in accelerated corrosion of the hull. The marina needs to have sufficient electrical isolation, and this can be provided by a decoupler.
The wharf's cathodic protection system is causing electrolytic corrosion on my vessel.
It is common for a vessel to switch its own cathodic protection system off and connect to the wharf's cathodic protection system. However, if the wharf's cathodic protection system is not operating satisfactorily, then vessel corrosion can occur. In this case, do not bond to the wharf!

Conclusion
Corrosion is a big problem in the marine environment, as the conditions are ideal and conducive to corrosion. However, there are systems available to mitigate corrosion, and these include materials selection, coatings, sacrificial anodes, and impressed current systems. Each has advantages and disadvantages, and corrosion engineers are kept employed by having to treat each new case on its merits.

Questions
Question time was lengthy and elicited some further interesting points.
Steel marine piles often have an HDPE sleeve and cap, and you get aerobic corrosion. If you can keep moisture out from between the sleeve and the pile, then the sleeve will do a good job. However, if you get a split in the sleeve, or the sleeve itself is not a tight fit and moisture is able to penetrate, then corrosion will result.
In some areas the waterway can be acidic due to engine exhausts exiting underwater, so what effect does this have on corrosion? If you use cathodic protection in that scenario, then you would need two or three times the usual current in order to mitigate the corrosion. In this situation a water analysis will be beneficial.
Wrought iron sometimes corrodes less than mild steel but not always. Some old wrought iron was a high-quality product, and formed its own crusty layer to protect, whereas steel doesn't. The old railway bridge at Ryde (now a walk-and-cycle way) is wrought iron which was totally imported and is still in business.
Some ships alongside a wharf switch off their own impressed current system and bond to the wharf. Many vessels are set to maintain a certain potential, either in seagoing or harbour mode, and the smarts in the system will try to maintain that potential. However, alongside the wharf, you want the wharf to provide most of the protective cathodic protection current, so that the wharf is protecting the ship, and you don't have the ship trying to protect the wharf!
Metal spray can be used to build up corroded surfaces in the tidal and splash zones, subject to careful surface preparation. Many bridges have had metal spray applied.
Tea staining is discolouration of the surface of stainless steel by corrosion. It is a cosmetic issue which does not affect the structural integrity or the lifetime of the material. Tea staining is a problem because it keeps recurring. It can usually be removed with warm soapy water, but you need to get to it early and keep at it.
Hinges and pins in the marine environment are often the subject of crevice corrosion, so what is the best material to use for these? Probably 316 stainless steel, although if graphite grease is used then the graphite will likely eat into the stainless steel!
The cutting edge in cathodic protection is on the side of smarts for control of impressed current systems. There is much regulation in the standards for testing several times per year. On the sacrificial anode side, it is purely a refinement of the standards; the Australian standard is 20 years old, but the DNV GL standard is much more recent. Impressed current anode materials mostly use a titanium substrate, and coatings are being asked to last longer and cost less. Changes are really more on the monitoring and hardware sides. Ceramic anodes for protection of concrete were tried a few years ago, but were not effective.
A lot of different polymers have been added to concrete to limit the ingress of moisture and block the electrolytic path. Many repair grouts are heavily polymer modified, but this makes them too resistive for subsequent cathodic protection, and their longevity is still unknown.

Jim Galanos (L) accepting the "thank you" bottle of wine and certificate from Geoffrey Fawcett
(Photo Phil Helmore)

The vote of thanks was proposed, and the certificate and "thank you" bottle of wine presented, by Geoffrey Fawcett.