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CORROSION IN BALLAST TANKS ON BOARD OF MERCHANT VESSELS

Corrosie in ballasttanks van koopvaardij schepen

In situ study of the significant parameters
In situ studie van de significante parameters

**Proefschrift voorgelegd tot het behalen van de graad van doctor in de Nautische
Wetenschappen aan de Universiteit Antwerpen te verdedigen door**

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Rust never sleeps

(Neil Young)

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"Als we wisten wat we deden, zou het geen onderzoek heten, toch?"

Albert Einstein

Thank you,

Scientific research is like sailing a ship from a port of departure to an unknown destination. You know where you are starting from but what the voyage will bring is always a surprise.

One thing is for sure, you cannot do it all by yourself and a good crew is indispensable to bring the voyage to a successful end.

The Antwerp Maritime Academy was my safe homeport throughout this journey. Every time I returned from a discovery excursion I found stability and the possibility to replenish my provisions.

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Preliminary remarks

In the course of our in situ research that started in March 2007 4 articles were forwarded for publication in A1 journals. After consultation of supervisors and co-supervisor, we preferred to reproduce the articles literally as published. Consequently, the data and corresponding regressions show a noticeable evolution. The first article was published in October 2009 and the last is still under review at the journal Nature. In March 2011 another article was published (not included in this thesis) in the context of the SSC symposium at the NACE conference in March 2011 based on an even more comprehensive dataset. These results were used in Chapter 10, the economical approach of the cost of corrosion. The number of ships surveyed increased from 65 in November 2009 to more than 140 in March 2011.

This way of publication results in occasional repetitions that were a necessary back up for the reader of the articles, spread out in time.

The articles were written by a team of specialists, based on our fundamental research material and initial conclusions, they provided the necessary scientific support. Since the articles were entirely copied their very technical exertions found a place in my PhD. The purpose is certainly not to assume credit for their intellectual efforts but to reflect the solid basis on which the conclusions are founded.

Subject of research

In literature a lot of evidence concerning corrosion problems in ballast tanks of merchant vessels can be found. Although this problem is not new (it arose the moment metallic elements in ship constructions were used), the corrosion phenomenon was accelerated over the last decennia, because of the double hull construction being imposed by the Oil Pollution Act following the Exxon Valdez catastrophe in Alaska. The background to this development, giving a description of the problem as well as its historical background, is represented in chapters 1 and 3 (detailing aspects of steel quality). A fundamental approach of the corrosion process is given as well, in chapter 2.

Based on my professional experience as master mariner I knew that maintenance in ballast tanks is a nightmare and only possible during lengthy and expensive dry-dock services. As such, the prime motivation for setting up this type of research was born.

The research questions that propelled me throughout this research project are in essence, threefold. Firstly, there is a more descriptive part, focusing on the construction of an in situ model for time-dependent corrosion. Indeed, while numerous lab experiments correlate the corrosion process to a single parameter, an in situ approach was selected for this work, because I'm convinced that no lab experiment is capable of grasping the totality of parameters influencing the degradation of the ballast tanks. If you start from reality it is easier and faster to deduce the critical decisive elements. The construction of this model and the methodology behind it are detailed in chapters 4 and 5 (which are also two of the scientific papers on which this Ph D thesis rests).

Secondly, I wanted to see through the corrosion mechanism and identify the prime factors favouring corrosion progression. Hence, from this model came a number of testable hypotheses concerning a number of operational or construction-related parameters. Chapter 7 describes for example the possible effect of coatings, area of operation, land of ship construction; chapter 9 focuses on the possible mitigating effect of sacrificial anodes. Each chapter is preceded by a technical introduction (respectively on coatings in chapter 6 and on anodes in chapter 8) to provide the reader with the necessary framework for these hypotheses.

Thirdly, I wished to be able to formulate achievable solutions founded on scientific solid field research in a clear way. This objective has come through in the discussion of chapter 9 (on the technical problems

regarding an effective use of anodes), but even more so in chapters 10 (where I present an economic analysis of three possible solutions for the corrosion problem) and 11 (listing several technical alternatives for ballast tanks as known today).

Chapter 12, in the end, gives an overall discussion of the results and conclusions, and proposes possibilities for future useful scientific research work.

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1. Introduction

1 Introduction

1.1 Ballast from an historical point of view

1.1.1 The need for stability drives the development of ballast

In essence, the need for ballast in a ship is a need to increase the draft, allowing the ship to be steered and propelled and to adjust the stability for any condition. A ship is called stable when it is able to right itself after being trusted to one side by an external force (Van Dokkum, 2010).

The initial stability of a ship is composed out of 2 parts: the "form stability" and the "weight stability". The weight stability is determined mainly by the position of the centre of gravity of the ship. This centre can be influenced by loading, discharging or repositioning of weights on board (Van Dokkum, 2010). For primitive boats the most important part was the "form stability" governed mainly by the shape of the water plane. Such open boats, however, offer very little protection to crew and cargo and are not very suitable for longer voyages. Increasing the volume of the ship to account for living quarters and cargo space without adding a significant amount of mass creates a vessel that floats on the water like an out of control balloon. Additionally, the use of sails as propulsion mechanism raises the centre of gravity of the ship and makes it less stable.

Both problems can be corrected by using ballast, which improves the "weight stability". The quantity of ballast a vessel requires is thereby determined by the volume of underwater ship, the minimum required draft and the position of the centre of gravity (Derret, 1983). As an example: the Norwegian Gokstad ship, with an empty weight of 20 ton, required about 10 ton of ballast. With all this, the draft was only half a meter. She could carry an extra 10 ton of cargo for only one foot of draft extra (Kito, 2007).

1.1.2 Dry material as ballast

The quest for ballast on board of ships started thousands of years ago. The first means of transportation over water were rafts, canoes, prawns, sailing without any ballast. These ships found the necessary buoyancy in the fact that they are very broad with a limited draft. The surface on which the upward force impacts was relatively big and, consequently, the weight carrying capacity was considerable.

In a first phase, abundantly available materials such as stones, rocks and sand were embarked as ballast materials. They were cheap and when not needed anymore, the materials were thrown overboard or used in some other way. The use of stones and other weights as ballast can be traced back to Egyptians, Phoenicians, Romans, and the Vikings. Although little information is available from ancient Egypt, it must be assumed that, because of their shallow keels, rather flat bottoms and enormous spread of sails, Egyptian boats could not have sailed light or they would have been in danger of capsizing. Larger vessels must therefore have been weighted with ballast of some kind. The ancient Egyptians may have used stones to provide the required stability, as found in the bilges of classical wrecks, but the cargo itself could also have served as ballast. On board of these primitive Egyptian ships the ballast occupied most of the available space beneath deck while the actual cargo was transported on deck, firmly lashed with ropes (Jones, 1995).

The inventory of the 8th century BC Phoenician ship wreck *Elissa*, discovered by Bob Ballard in 1999, mentions the presence of 6 ballast stones (Ballard, 2002). Phoenician war vessels, on the other hand, had no need for any form of ballast, as these ships were always loaded with a constant number of rowers (Coates, 1987). Similarly, 29 millstones were discovered aboard the *Kyrenia*, a 4th century BC wreck of a Greek merchant ship discovered by Andreas Cariolou in 1965. These millstones were on board as cargo but at the same time served as ballast (Katzev, 2007).

Not only stone served as ballast material: rocks, sand, bricks and roofing tiles were used among other materials. A Byzantine wreck of a 15-m-long ship found at Serçe Limani on the Asia Minor coast, sunk in 1020, carrying a large amount of glass cullet (2 tons of raw glass and 1 ton of broken glassware and glassmaking waste). The transport of glass cullet was an economically and technically sound operation, as fabrication of new glass departing from fragments of broken glass is cheaper and easier than starting from raw material (Van Doorninck, 2002). A similar strategy was adhered to throughout medieval times, until recently. Part of the ballast load was permanent, while another part was adapted in function of the cargo and the position of the weight on board. To cite a contemporary author, Hakluyt R. (1584): "This afternoone we tooke in two or three skiffes lading of stones to ballast our shippe withall. It hyeth here four foot water, and floweth by fits, vncertaine to be iudged".

On board of military ships the quantity of ballast could be reduced due to the presence of heavy cannons. However, the presence of a large arms

complement did not always guarantee sufficient stability. The most tragic example is undoubtedly the Swedish warship *Vasa*. Around 4:00 PM on August 10th, 1628 she set sail in the Stockholm harbour on her maiden voyage. After sailing about 1,300 meters, a light gust of wind caused the *Vasa* to heel over on her side. Water poured in through the gun portals and the ship sank with a loss of 53 lives. Although the maximum amount of ballast was loaded on board, it was apparently inadequate to compensate for the great size and weight of the masts, sails and guns (Erling, 2008 & Young, 2002).

A similar story can be told about the *Mary-Rose*, one of Henry VIII's 'great ships'. The ship possessed the then recently invented gun ports, and, after undergoing a significant refit in 1536, she was also one of the first ships that could fire a broadside (Rule, 1983 & Bell et al., 2009). Upon engaging the French armada on July 19th, 1545, having fired a broadside at the enemy and turning to fire the other broadside, the *Mary Rose* capsized, with water flooding into her open gun ports. Why the *Mary Rose* capsized is still unknown. Maybe the ship was overloaded with extra soldiers. Some reports say there was a breeze that sprang up suddenly. A freak wave is suggested as well as one of the possibilities (Liu, P.C., 2007).

Figure 1 gives a good idea of the position of ballast rocks on board of a galleon, used to lower the centre of gravity (Callahan J.E., 2001). Galleons were large ocean going sailing ships used from the 16th till the 18th century.

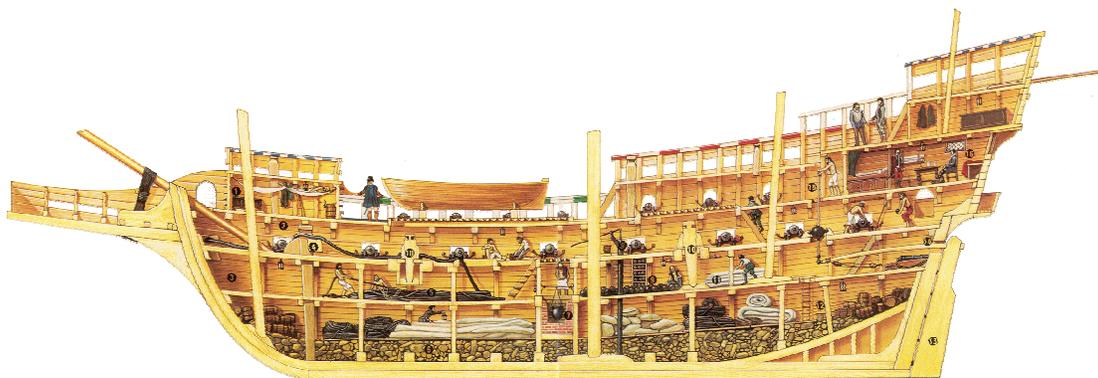


Figure 1: Longitudinal section of a galleon (Rutland et al., 1986)

The use of such dry materials has continued until early 20th century (Ruiz, M.G. et al., 2003). The first paving materials in Wilmington, NC USA were ballast stones. Conveniently discarded by departing vessels, the endless supply of stone was also used for house foundations, retaining walls and filler when Water Street was created out of the marshy waterfront (Tetterton, 2005). Less conventional ballast material consisted of mummified Egyptian cats from Bubastis and Stabel Antar, which were so numerous that they were used as ballast for ships going back to Europe, where they were used as fertilizer (Ikram 2005). During the American Civil War, a Yankee sea captain trading in the Mediterranean docked at Alexandria, Egypt, with a half-empty ship. He bought the statue of Nedjem, along with some other sculptures, to serve as ballast (Institute of Egyptian Art & Archaeology, 2010).

1.1.3 The use of seawater ballast

Shifting from dry matter to seawater as ballast was a logical evolution. Sea water is always present in abundant quantities, free and easily handled by means of pumps.

Ballast tanks are an invention of the 19th century. The first ships using water as ballast were the clipper ships, at that time the fastest sailing vessels. Those ships had a metal tank in the middle that could be filled with seawater, when necessary. In the 1850's a number of vessel designs were proposed with removable ballast tanks. These were simply bolted to the floor of the hold and removed when cargo capacity was required (Safinah, 2009).

In the same decade ships with integrated built-in tanks solely used for ballast appear. John Henry Sangster Coutts was a shipbuilding pioneer who built the S.S. QED, in 1844, the first ship equipped with a double bottom, enabling her to carry water ballast in double bottom tanks, instead of loose sand in the holds (Newsguardian, 2009).

In 1906 the Augustus B. Wolvin was launched. She was the first ship to be equipped with ballast tanks along her sides, sandwiched between the hull plating and the cargo hold below the deck arches (Tompson, 1994).

1.2 The use of metal in ship-construction

In parallel with the search for a suitable type of ballast, shipbuilding has undergone another radical transition: from wooden to iron constructions.

1.2.1 Ancient times

Sun, rain and humidity, the natural habitat of any ship, are very malicious elements. The Egyptian Khufu Solar boat (Kadry, 1986) may well have survived 4,000 years without problems thanks to the very dry atmosphere of the tomb in which it remained closed up for all that time; other ships were spared less and decayed relentlessly under the influence of the hostile marine environment.

Faced with the need to keep their ships in optima forma, shipbuilders have therefore been looking for ways to combat this environment. The earliest evidence of the use of metal in ship building goes back to the 4th century BC. In those days, Greek culture and technology dominated the eastern and central Mediterranean while Rome began to gain force on the Italian Peninsula. A wreck site from this period, found off the shores of Kyrenia (Cyprus), offers a great deal of insight into the general nautical features in the Mediterranean of those days (Steffy, 1985): shell-first construction, planking fastened together by locked mortise and tenon fastenings and framing mostly fastened to the planking by metal nails (Kahanov, 2004).

The shell-first technique involves constructing the "shell" of the boat first, and laying in the framework last. This particular construction technique relied extensively on structural support provided by peg-mortise-and-tenon joinery through the "shell" of the boat. This method of ship construction appears to have originated from the seafaring nations of the Mediterranean (Bellwood, 2007).

At first, mortise and tenon joints were used together with sewn fastenings. Later on, with the improvement of woodworking techniques in the Eastern Mediterranean Sea basin, the technique of locked mortise and tenon joints could be applied as the sole plank fastening method in the hull. Also, the subsequent change to metal-fastened frames instead of being lashed needed better skills in the way the timber was elaborated. The application of both techniques increased the strength and the water tightness of the planking shell (McGrail, 2006). On top, Roman shipbuilders added a sheath of lead on the hull below the water line to protect it from marine wood-boring worms (Frost, 1972 & Rosen and Galili, 2007); this practice was lost after the fall of the Roman Empire, and was revived only in the 18th century.

1.2.2 Transition from wood to metal

For several centuries, sailing ships were constructed most prominently out of wood and according an unvarying design. It was said that a sailor from the Spanish Armada (1588) could step on board of one of the 19th century sailing ships and take up his duties (Gould, 2001).

The transition from wooden to metal ships has been slow. Wooden ships were restricted in length because a lack in longitudinal rigidity. Wooden frames and braces were bulky stealing a lot of volume from the earning cargo. Stimulating factors for this transition were the shortage of decent construction wood after the big fire in London 1666 and the repercussions on the timber prices (Newland, 2007) as well as the military consideration that a metal hull was more resistant to a cannonball than a wooden fuselage.

1.2.3 Composite hulls

Composite hulls were a combination of the strength of iron frames and the durability of a wooden hull (with wood being more resistant to seawater than iron, while the salt in the sea water acts as a natural biocide extending the life of the ships). A copper sheathing was added for extra protection and anti-fouling purposes. A famous example of this generation of ships is the "Cutty Shark". The Cutty Shark was designed by Hercules Linton and built in 1869 at Dumbarton, Scotland, by the firm of Scott & Linton, for Captain John "Jock" "White Hat" Willis. Since 1954 she is berthed in Greenwich as a museum ship.

Tea clippers were the racing horses of the last part of the 19th century. They had 3 or more masts and a square rig.

The construction of the composite ships was based on the design of full wooden ships. First, the size of the wooden internal components was reduced and the loss in strength was compensated through the addition of metal elements, such as iron plating bolted to the beams. Consecutively, metal girders would replace the wooden elements altogether.



Figure 2: Composite hull structure of the Cutty Shark (Kentley, 2004)

1.2.4 17th and 18th century

The protection of the immersed part of the ship has been a constant source of concern. A rich variety of material and substances has been used ranging from wood, cement, leather, rubber, glass, plaster to finally metal. In the 17th and 18th century lead was used to protect the wooden hull, albeit with variegated success.

However, the increasing use of metal aboard seafaring vessels produced other challenges. The galvanic effect, at that time hardly understood, made other metal elements on board disappear in a very mysterious way.



Figure 3: Rudder irons (Maritime museum Rotterdam, 2010)

In 1677 and 1678 Sir John Narborough and Sir John Kempthorne complained that the rudder irons of the "Plymouth" and "Dreadnought" were so much eaten as to make it unsafe for them to go to sea; and in 1682 similar complaints were made of the effects of lead in contact with iron (Charles, 1867).

We have to wait till the 19th century before this electrochemical phenomenon was understood and defeated. The first application can be traced back to 1824, when Sir Humphry Davy, in a project financed by the British Navy, succeeded in protecting copper sheathing against corrosion from seawater by the use of iron anodes. The protection of the copper

sheathing with sacrificial anodes became traditional. When wooden ships were pushed aside by iron ships this practice continued. The iron anodes were replaced by zinc slabs. It was the general opinion that these zinc anodes were ineffective, although the anodes offered limited protection against local galvanic effects mainly due to the presence of the bronze propeller (Roberge, 2008).

1.2.5 19th century, full metal ships

It took till 1870 before the composite hull ships were abandoned in favour of the full metal hull ships. This would not have been possible without the invention of the puddle process by Henry Cort¹ in 1784.

The puddle process is a technique used to remove the carbon impurities and convert cast iron² into wrought³ iron making it strong, workable and cost effective (Encyclopaedia Britannica, 2010).

Steel, containing between 0.2 and 2.1 percent carbon, often with other constituents such as manganese, chromium, nickel, molybdenum, copper, tungsten, cobalt, or silicon, is less pure than wrought iron, but purer than cast iron. It can be both forged and cast (Encyclopaedia Britannica, 2010).

But in Cort's day there was no cheap process for making steel on a large scale. We have to wait till 1856 when Bessemer patented the process of refining molten iron with blasts of air in a Bessemer furnace, or converter.

However, three characteristics of iron ships led many naval engineers to oppose ships entirely made of iron: (1) the magnetic properties of iron, affecting compass accuracy, (2) the vulnerability to corrosion, especially in a marine environment, and (3) the increased chance of being struck by lightning at sea due to the incorporation of iron-clad masts (Ville, 1993). Decks and structural elements such as deck machinery, including capstans, windlasses, anchors, chains, and other ground tackle could be found in identical form on wooden, composite, and iron ships (Souza, 1998).

¹ Henry Cort: (1741? – May 23, 1800) was an English ironmaster. During the Industrial Revolution in England, Cort began refining iron from pig iron to wrought iron (or bar iron) using innovative production systems.

² Cast Iron: an alloy of iron that contains 2 to 4 percent carbon, along with varying amounts of silicon and manganese and traces of impurities such as sulfur and phosphorus.

³ Wrought iron: Wrought iron is a soft, easily worked, fibrous metal. It usually contains less than 0.1% carbon and 1 – 2% slag. It is superior for most purposes to cast iron, which is hard and brittle because of its higher carbon content.

Metal was not only used for the construction of the ship's hull but was also applied in the standing rigging of the sailing ships. The use of iron wires, linked iron rods and less bulky masts resulted in a considerable weight advantage, improved stability and less maintenance (Greenhill, 1993).

The first iron ship to go to sea was the Aaron Manby, ordered by a society formed by Charles Manby and Captain Charles Napier in 1821 at the Horseley Ironworks (Staffordshire, England) and owned by Aaron Manby (Haws, 1988). After her maiden trip she was mainly engaged as a river barge on the River Seine and the Loire River at Nantes. She was scrapped in 1855 (McCarthy, 1985). In fact, the general opinion at that time was that such a vessel could sink the moment it was launched. Nevertheless, the vessel was fabricated and then assembled at Rotherhithe on the River Thames. Contrary to the prevailing wisdom of the day, the flat-bottomed, 120-foot iron-hulled vessel not only floated, but it drew about a foot less water than the wooden steamboats anchored around it. The first iron ship to be classified by Lloyds register was the "Ironsides" in 1838 (Martin, 2005 & Donahue, 2010).

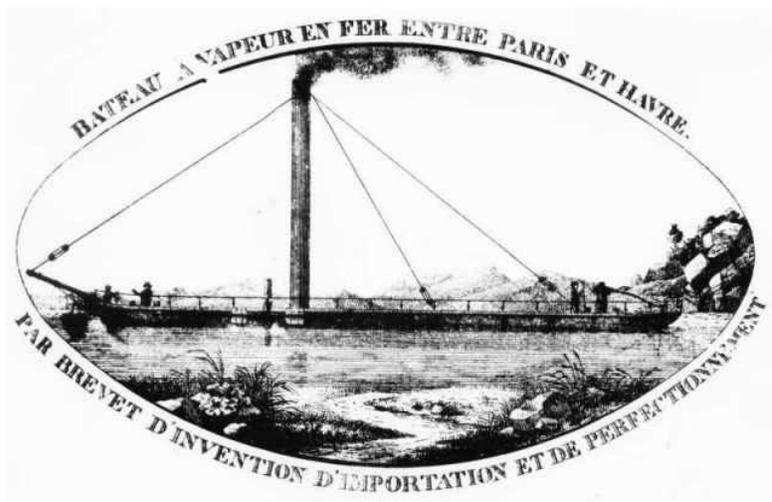


Figure 4: The Aaron Manby (Haws, 1988)

1.2.6 Ironclad ships

A transitional stage between wooden and iron ships are the "ironclad" battle ships, typical 19th century wooden military ships, armoured with very thick metal sheaths.

The first oceangoing ironclad was the French battleship "La Gloire". She was designed by the French naval architect Dupuy de Lôme, and was launched at the arsenal of Mourillon, Toulon, on the 24th of November 1859. Two sister-ships were built.



Figure 5: La Gloire (Musée national de la marine, 2010)

The English reacted by building the “HMS Warrior”, ordered in June 1859. Although Sir John Pakingham, the First Lord of the Admiralty, supported the idea of a hull completely wrought out of iron, an ironclad ship was ordered.

The ship was a 5,630-ton broadside battleship cut down by one deck in order to save weight. She was protected by massive 12 cm thick iron protection plates sheathed over a wooden hull structure, backed with 43cm of timber, and was able to withstand the experimental firing of the strongest guns of the time (Wells, 1987). The fuselage was completely constructed out of iron and reinforced with armoured plates over a length of 61m amidships. Decommissioned in 1883, the HMS Warrior is actually in use as a museum ship at Portsmouth Historic Dockyard (Hill, 1995).



Figure 6: H.M.S. Warrior (National Maritime Museum, 2010)

The Great Eastern

The climax of iron ship building is without any doubt the “Great Eastern” of Isambard Kingdom Brunel⁴ built by J Scott Russell & Co. at Millwall on

⁴ Isambard Kingdom Brunel, (9 April 1806 – 15 September 1859), was a leading British civil engineer, famed for his bridges, dockyards, the first major British railway and a series of famous steamships, including the first propeller-driven transatlantic steamship.

the River Thames, London. She was by far the largest ship ever built at the time of her launch (in 1858), and had the capacity to carry 4,000 passengers around the world without refuelling. Her length of 692 feet (211 m) was only surpassed in 1899 by the 705 feet (215 m) 17,274 gross ton RMS Oceanic, and her gross tonnage of 18,915 was only surpassed in 1901 by the 700 feet (210 m) and 21,035 gross ton RMS Celtic. Brunel knew her affectionately as the "Great Babe" (Winser, 2010).

Photo # NH 91964 Engraving of S.S. Great Eastern

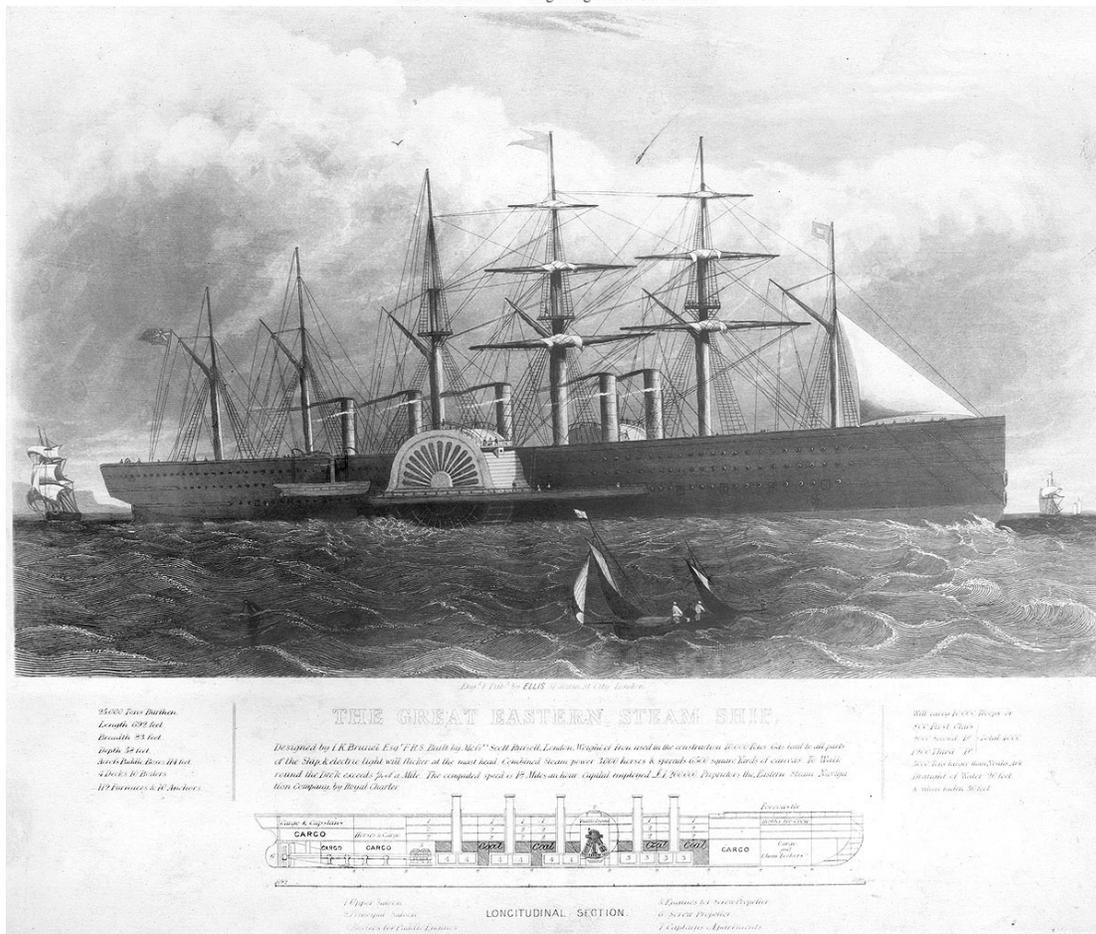


Figure 7: The Great Eastern (U.S. Naval Historical Centre Photograph, 2010)

The Great Eastern was constructed with a double hull with approximately 90cm between the outer skin and the inner plating. The ship had 16 watertight compartments making her nearly unsinkable. The demolition (1888-1890) of this ship was so labour-intensive that the scrap yard nearly went bankrupt.

Steel hull ships

A logical continuation of the iron hull ships are the steel hull ships. Iron becomes steel when the impurities are removed and the carbon concentration varies between 0.2 and 2.1% by weight. The biggest

advantage of steel over iron is an improved strength allowing a reduction in light ship⁵ and consequently an increase in cargo carrying capacity.

The first known steel was probably produced accidentally by the primitive method which melted wrought iron direct from the ore. The increase of the degree of heat in the primitive smelting furnace caused the iron to become hot enough to absorb in a combined form that quantity of carbon which gave it a new property. It was found that, although this newly discovered grade of metal had to a greater or less degree the malleability of wrought iron when cooled slowly, it further had the property of becoming hard and brittle when cooled suddenly from a red heat (Danforth, 1912).

The industrial production of steel is a realization of the British inventor Bessemer (1813-1898). In 1856 Bessemer took a patent on a process for cheaply and rapidly converting pig iron into steel (Britannica Concise Encyclopaedia Online, 2010). The process was refined by Alexander Lyman Holley during the Civil War.

The world first steel ship was the "Ma Roberts" built in 1858 on the Laird shipyards in Birkenhead. The ship was ordered by Dr. David Livingstone for his expedition on the Zambezi. The "Ma Roberts" was not a successful design. She was so slow that a native canoe could easily outdistance her and she burned so much fuel that half of the time was given just to cut wood for her (CCN, 2003).

Rivets and welding

Riveting was the common technique to join ship plates till the beginning of the 20th century.

Riveted ships were strong and durable but the process of riveting had drawbacks. The main problem was the time needed to align steel plates and drill holes for rivets, and to set and drive home the rivets. To place each rivet (150,000 for a typical hull) took two workers, one on either side of the plates being fastened, and two more to do the necessary preparations. A "driller" had to position each hole in the proper place and drill through the one-inch-thick hull plate. After the plates were aligned on the frames they seldom matched the pre-drilled holes precisely, so a "reamer" had to enlarge the holes to eliminate overlap and allow the rivet to fit. The weight of the rivets, needed to hold the ship together, was substantial and could be more than 300 tons. The rivets, unless they were

⁵ Light Ship: The weight of the vessel completely ready for service in every respect, including permanent ballast, spare parts, lubricating oil, working stores, plus an allowance for the crew and their personal effects. No fuel, fresh water, ballast or cargo or any other item is loaded.

flush with the hull plate, increased the hydrodynamic resistance (Bonnett, 2000).

Welding ship plates was introduced at the end of WW I. In 1918 the British Admiralty tested metal-arc welding on barge AC 1320 and Lloyds Register permits the use of metal-arc welding in the main structure of ships (Sapp, 2010). The first ship to be designed with an all-welded hull was the MS Fullagar, which hull was laid at Cammell Laird in 1920 (Haws, 1988).

During WW II the demand for merchant vessels was insatiable. German U-boats were foundering ships at an incredible rhythm. Without sufficient new ships the supply lines to Europe would be endangered.

The most famous examples of this cannon fodder were the Liberty ships. In the earlier days of the construction, it took about 230 days to build a Liberty Ship. Already impressive, construction time was actually reduced to an average of 42 days. The record for Liberty Ship construction was held by the building of SS Robert E. Peary, which was launched 4 days, 15 hours, and 30 minutes after the keel was laid, although this record was by far the exception; much of the fitting-out work remained to be done after launching, and as expected, no other Liberty Ship came close to this record. By 1943, three Liberty Ships were being launched every day (Chen, 2004-2010 & Pearsall, 1994).

Eighteen American shipyards built 2,751 Liberties between 1941 and 1945, easily the largest number of ships produced to a single design.



Figure 8: The Jeremiah O'Brien (Maskell, 1994)

It was the general opinion that these ships were not built to last. This idea was proven very wrong. The Liberty class kept on sailing in the merchant navy till the end of the 20th century. Even at this moment two of these ships are still active, one of which is the Jeremiah O'Brien (Aris, 2007).

Since World War II, ship building principles and materials have remained unchanged. Larger and more standardized vessels have been built relying on prefabricated modules, and welding techniques and skills have improved significantly.

Recently high-strength corrosion-resistant nitrogen-alloyed steel grades were developed allowing a weight reduction of the light ship and consequently an increase in cargo carrying capacity. Owing to their physicochemical characteristics, titanium alloys, aluminium and zinc became common use in marine facilities.

At this moment the use of various kinds of fibreglass plastics is restricted to the construction of pleasure craft, fishing boats, military ships and high speed craft. Fibreglass plastics are strong, cheap and easy to work with. Their main advantage is chemical and biological stability. A further realistic development is the use of so called "sandwich" plates with high-tensile steel or fibreglass outside layer and polymeric or low-tensile composite interlayer. Lloyds register published in 2006 the Provisional Rules for the Application of Sandwich Panel Construction to Ship Structure (Eyres, 2007). The main advantages of the Sandwich Panel System are a simplified fabrication, better design features, reduced weight cost, damping characteristics, improved operational performance, resistance to extreme loads and excellent fire resistance properties (Welch, 2005).



Figure 9: Sandwich plate (Welch, 2005)

1.3 The ballast tank configuration on board of modern ships

1.3.1 The basic ballast tank configuration

Ballast tanks are separated tanks only to be used for the transport of ballast. Figure 10 shows the forepeak tank (FP) and after peak tank (AP) present on board of nearly all ships.

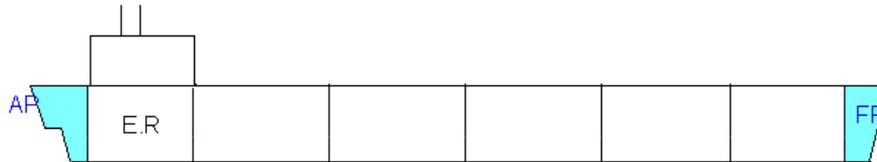


Figure 10: Forepeak and after peak tank (own work)

The division of the other tanks on board is function of the type of ship (figure 11). General cargo ship and container carriers only have double bottom tanks, bulk carriers have double bottoms and topside tanks, and on board of tankers, the double hull space is pre-designated to contain segregated ballast. These layouts are not coincidental. Tankers and bulk carriers sail in ballast for an important part of the time; on board of these ships a lot of ballast capacity is present.

Containers and general cargo ship nearly always have cargo on board and consequently carry less ballast.

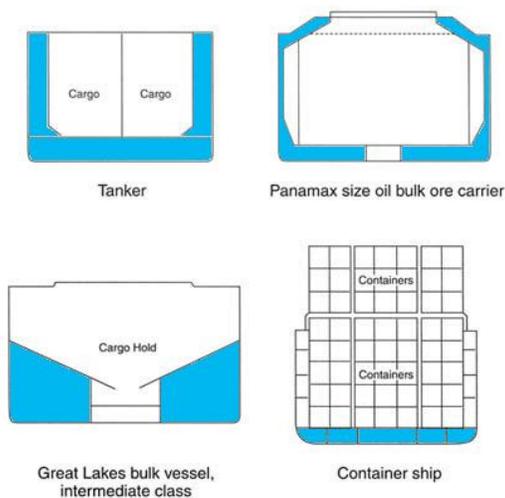


Figure 11: Different ballast tank configurations (National Research Council, 1996)

Hence the ballast capacity is limited and the main function of the ballast is to control the trim, list, stability and the stress on the ship.

1.3.2 Ballast equipment

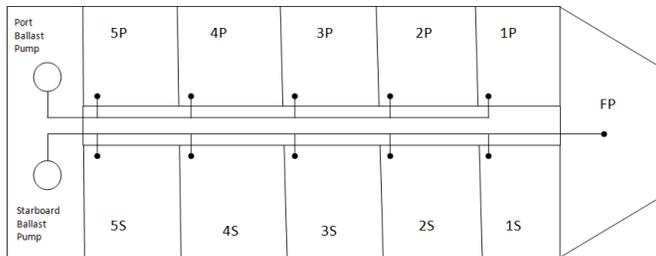


Figure 12: Ballast bottom line configuration – own work

The equipment to load and discharge ballast consists out of a number of pumps and a pipeline system (figure 12). In general the pumps are installed in a pump room or in the engine room of the ship. The bulk quantity is moved by means of centrifugal pumps while the stripping is done with piston pumps or ejectors.

Deepwell⁶ pumps (figure 13) are being used on board of tankers over more than 40 years. Recently this pump type is also used in ballast tanks. Since the driving unit is installed on deck the need for a separate pump room disappears. These immersed pumps also have better stripping qualities.

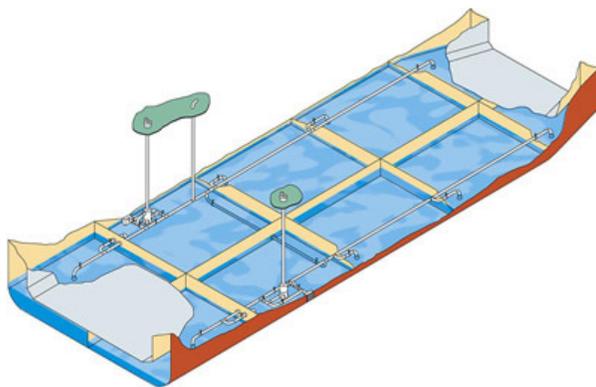


Figure 13: Submerged ballast pumps (Framo, 2010)

⁶ A deepwell pump is a submersible pump that is designed and manufactured specifically for being submerged within a tank. Typical for a deepwell pump is that the drive mechanism is installed on deck.



Figure 14: Bulk carrier discharging topside tanks (Bolton, 2010)

Bulk carriers discharge the ballast out of the topside tanks by means of drop valves⁷ (figure 14).

Filters are provided on the intake to block unwanted objects.

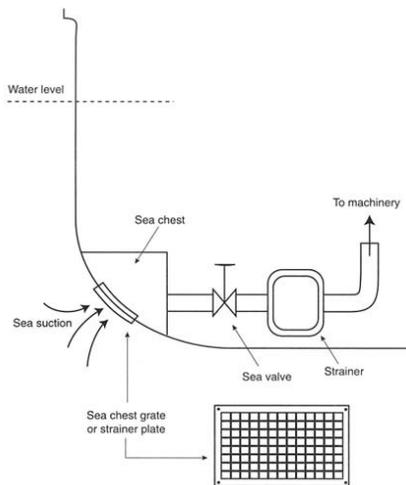


Figure 15: Ballast water intake (NRC, 1996) & Figure 16: Tank suction - own work

The quantity of ballast on board (figure 17) depends upon the type of the ship. Generally speaking the ballast quantity is approximately 30 to 40% of the summer deadweight, being the weight on board when the ship is loaded to her summer marks.

⁷ A drop valve is an overboard valve providing the rapid and free discharge of the ballast from the topside tanks on board of bulk carriers without using pumps.

Ballast Needs ^a	Vessel Types	Typical Pumping Rates (m ³ /h)
Ballast replaces cargo Ballast required in large quantities, primarily for return voyage.	Dry bulk carriers	5,000–10,000
	Ore carriers	10,000
	Tankers	5,000–20,000
	Liquefied-gas carriers	5,000–10,000
Ballast for vessel control Ballast required in almost all loading conditions to control stability, trim, and heel.	Oil bulk ore carriers	10,000–15,000
	Container ships	1,000–2,000
	Ferries	200–500
	General cargo vessels	1,000–2,000
	Passenger vessels	200–500
	Roll-on, roll-off vessels	1,000–2,000
	Fishing vessels	50
	Fish factory vessels	500
	Military vessels	50–100
	Float-on, float-off vessels	10,000–15,000
Ballast for loading and unloading operations Ballast taken on locally in large volumes and discharged in same location.	Heavy lift vessels	5,000
	Military amphibious assault vessels	5,000
	Barge-carrying cargo vessels	1,000–2,000

^a The three categories of ballast needs are not mutually exclusive. For example, a vessel in which ballast replaces cargo may also require ballast to control stability.

Figure 17: Ballast needs and pumping rates of different ship types (NRC, 1996)

1.4 Tankers and ballast (tanks)

1.4.1 The pre-MARPOL problem of dirty ballast

Tankers and ballast always had a very difficult symbiosis. Before 1950, a surveyor came on board of an oil tanker after the oil cargo had been discharged. He looked into the tanks, declared them empty and confirmed this by means of an empty tank certificate. Any cargo leftovers were considered impossible to pump out and were allowed to remain on board.

After the empty tank certificate had been signed, ballast was embarked into the oil tanks, leading to a severe contamination of the ballast water: on top of the water floated a layer of the leftovers of the oil, in the form of sticky brown, green or black substances. This ballast water was known under the name “dirty ballast”, which, in those days, was discharged unscrupulously into the coastal water of the loading port.

In time, however, coastal nations would start to demand of tankers to arrive in the loading port with cleaner ballast. To comply, the tankers would discharge the dirty ballast water in open sea and load fresh water into the cleaned tanks. This last type of ballast was called “clean ballast” and the tankers handling their ballast this way are known as “pre-MARPOL tankers”. Evidently, this shifted the pollution problem from the coastal waters to the open ocean.

1.4.2 OILPOL 1954

The potentially devastating effect of oil on the marine environment was soon recognized, in 1954, by the International Convention for the Prevention of Pollution of the Sea by Oil (OILPOL 1954). OILPOL 1954 sets out some of the basic principles on how to handle oil waste, preventing the pollution of the marine environment by hydrocarbons. The maritime water was to be divided into normal and special areas. In the special areas no discharges were allowed, while in the other zones a limited quantity of oil could be discharged, as long as a number of criteria were observed, such as a maximum concentration.

1.4.3 MARPOL 73/78

The International Convention for the Prevention of Pollution from Ships, MARPOL 73, took over the foundations of OILPOL and tightened the reins.

Even before MARPOL 73 entered into force some major oil pollutions showed that the 1973 version was ineffective. In 1978, during the Tanker Safety and Pollution Prevention conference (TSPP 78) important measures were taken to improve the efficiency of the impending regulation. The outcome of this conference was the 1978 protocol amending MARPOL 1973. Since then the marine pollution convention is known under the name MARPOL 73/78.

One of the imposed measures was the compulsory use of “segregated ballast” on board of tankers. Segregated ballast means that the ballast water is loaded into a tank that is completely separated from the cargo oil- and fuel oil system and that is permanently and solely allocated to the carriage of ballast (Code of federal regulations, 2010).

Figure 18 illustrates the difference between pre-MARPOL tankers and segregated ballast tankers. On board of the pre-MARPOL only a few permanent ballast tanks were provided for trimming purposes. The bulk quantity of ballast was taken into the cargo tanks.

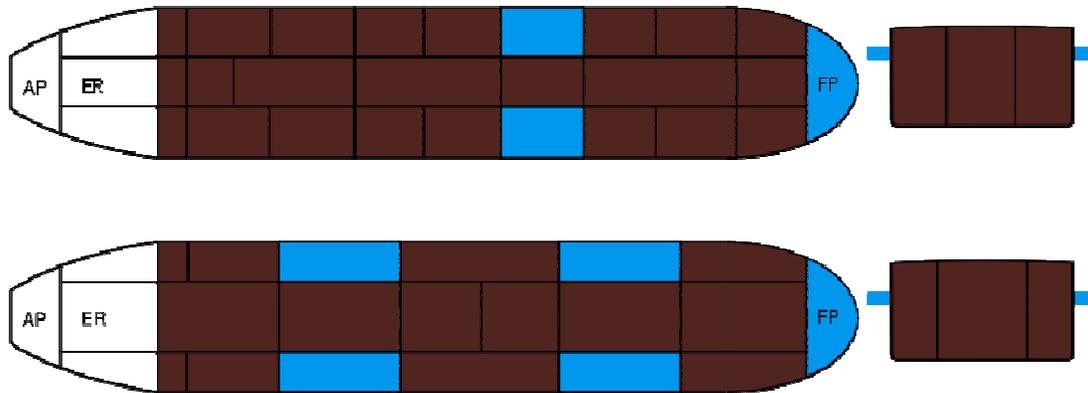


Figure 18: Pre-MARPOL en MARPOL tanker (segregated ballast tanker) – own work

The 1978 MARPOL Protocol introduced the concept known as protective location of segregated ballast tanks (figure 19). This means that the ballast tanks (which are empty on the cargo-carrying leg of the voyage and only loaded with water ballast for the return leg) are positioned where the impact of a collision or grounding is likely to be greatest. In this way the amount of cargo spilled after such an accident will be greatly reduced (IMO, 2010).

30% of the surface of the cargo tanks had to be protected by a ballast tank.

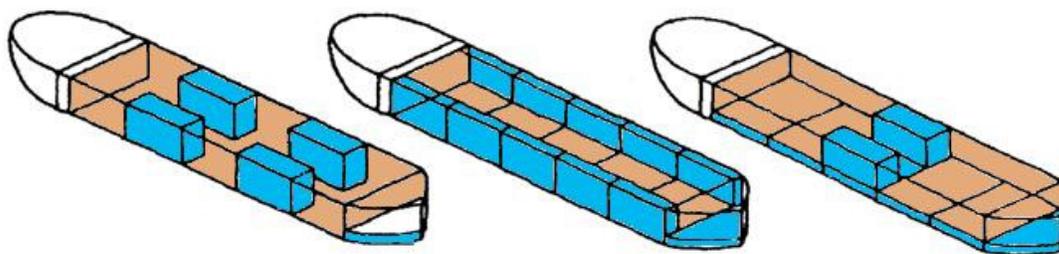


Figure 19: Protective location of ballast tanks – own work

All of the 3 designs in figure 19 are satisfying the 30% rule.

MARPOL 73/78 imposes the use of segregated ballast on board of all tankers > 20.000 DWT. On board of tankers built after 1978 this new element could be incorporated.

For the existing tankers at that time a transition regime was provided. Two alternatives were possible: The application of crude oil washing in the clean ballast tanks or the use of “dedicated clean ballast”. A dedicated clean ballast tank means a cargo tank that is allocated solely for the

carriage of clean ballast. Nevertheless, dedicated clean ballast was banned in April 2005. From that moment onwards, all ballast had to be segregated and located to minimize damage caused by collision or grounding. MARPOL tankers (SBT-tankers) were phased out in 2010 with an extension possible till 2015.

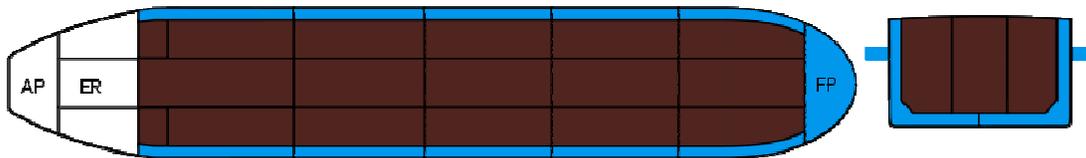


Figure 20: Double hull tanker – own work

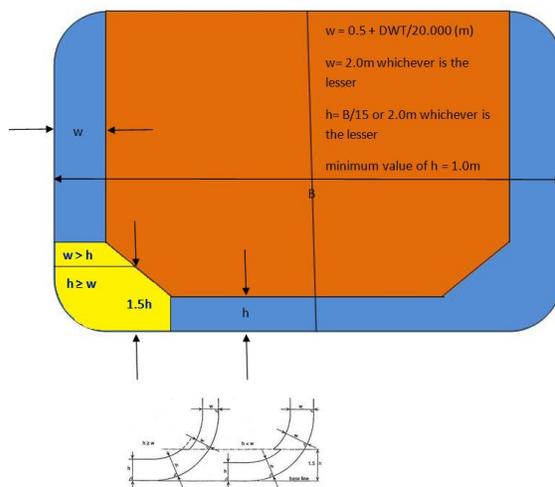


Figure 21: Dimensions of the double hull structure (IMO, 2010)

From 2010 (2015) all tankers used for the carriage of crude oil have a double hull (figures 20 & 21).

Double hull doesn't necessarily mean that the segregated ballast tanks have to be installed inside that double hull space.

NKK, Nippon Kaiji Kyokai, the Japanese classification society, projected a very large crude carrier (VLCC), keeping the double hull spaces dry and providing separate segregated ballast tanks on board.

The main purpose of this concept was to fight the corrosion problem in double hull ballast tanks.

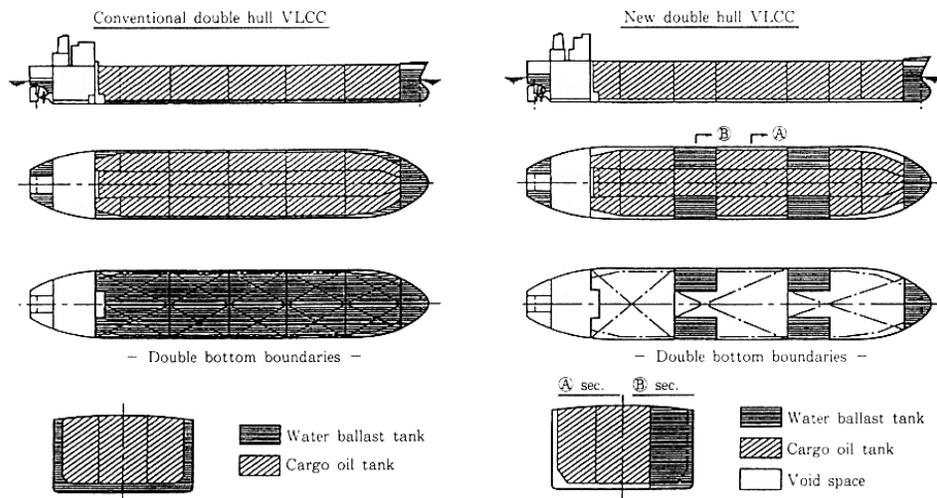


Figure 22: NKK void double Hull VLCC. (Takehiko, 1996)

1.4.4 MARPOL Annex I, alternative solutions

Regulation 19 of MARPOL Annex 1 provides two equivalents for a double bottom construction. Firstly, there is hydrostatic balanced loading (HBL; figure 23).

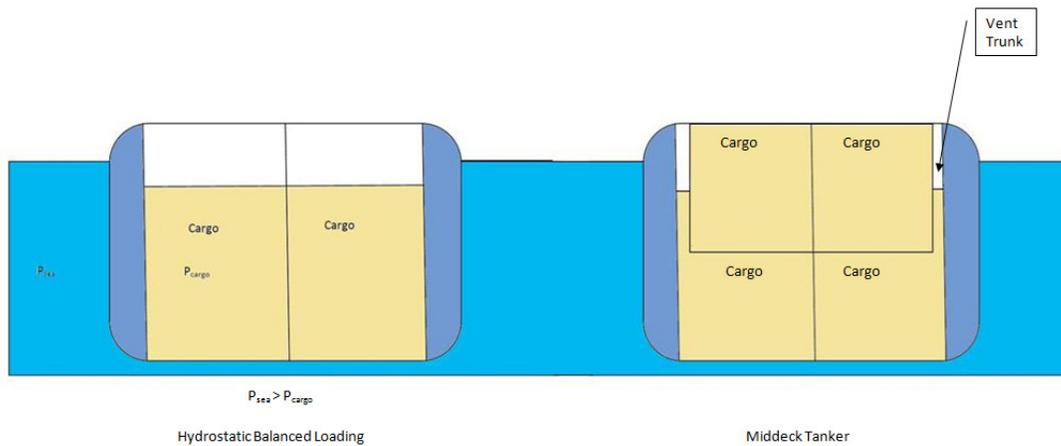


Figure 23: Hydrostatic Balanced Loading and Mid-deck Tanker (Haikiri, 1992)

This methodology limits the height of the cargo in the cargo tanks so that the hydrostatic pressure inside the tank is always smaller than the hydrostatic seawater pressure. In case of leakage the seawater will seep in and the cargo will not escape to the sea. Secondly, tankers can be constructed with a mid-deck, protecting the lower tanks hydrostatically while offering the upper tanks the advantage of the double hull.

Another particularity of MARPOL regulation 19 is that International Maritime Organization (IMO) accepts alternative solutions as long as they

offer the same guarantees as a classic double hull construction. However, up till now only one variant on the double hull construction has been evaluated and approved: the Coulombi Egg tanker design (figure 24). This design was developed by Heiwa Co and Mr Anders Björkman, M.Sc., Naval Architect, 1990-1997. The aim was to reduce accidental pollution in case of grounding and collision compared to a normal double hull design.

The basis of the concept is a single hull mid-deck tanker with halfway up a cofferdam and a sloping crumple zone insuring a same rigidity as a double hull structure.

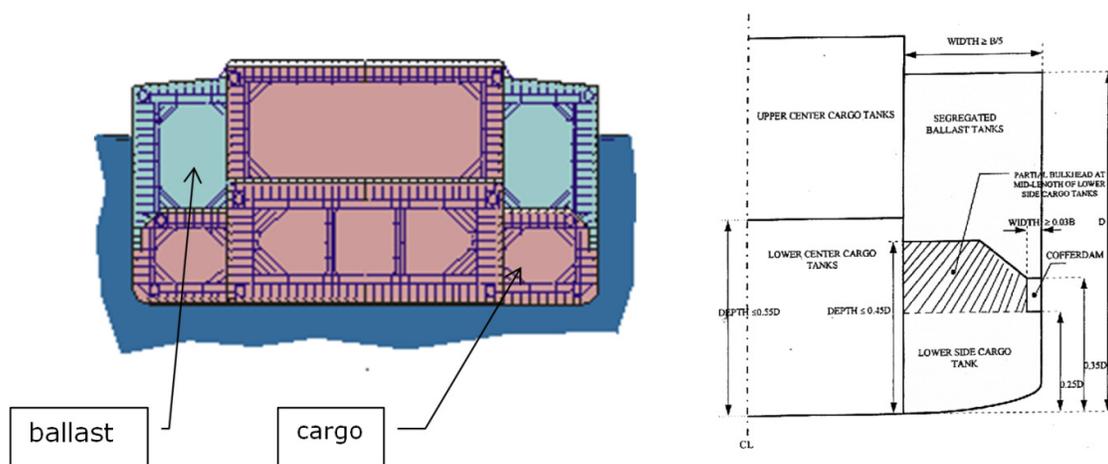


Figure 24: The Coulombi Egg Design (Heiwa, 2010)

It has been sufficiently proven that a Coulombi Egg design is superior to a classic design when it comes to pollution and fire/explosion in case of grounding and collision. Up till now the United States Coast Guard, in accordance with the Oil Pollution Act (1990), did not approve the Coulombi Egg tanker for operation in the US waters, as it fails to meet zero emission requirements (in case of grounding, a small amount of oil will be lost). There are also some concerns regarding the structural complexity and the use of voids/trunks, which can increase cost & decrease cargo capacity (NRC, 2001).

1.5 The problem of corrosion in segregated ballast tanks

The degradation of metallic surfaces due to atmospheric corrosion is a well-known problem for many exposed steel structures such as bridges, storage tanks and pipelines. Bringing sea water into this equation causes an even more aggressive environment, and an increased corrosion effect. Nevertheless, merchant marine vessels, carrying cargo all over the seven seas, will make good use of this abundant commodity when necessary: in the absence of cargo, or when the ship is only partly loaded, she carries seawater in her ballast tanks to ensure manoeuvrability and to control draft, stress and stability. As necessary as they are for the operation of a ship, though, the fact that ballast tanks are prone to corrosion, poses a distinct problem for a ship.

First of all, corrosion is expensive. For the U.S. economy alone, the 1998 cost of corrosion amounted to \$275.7 billion/year (CC. Technology & NACE International). These economic losses were provoked by production interruptions, incidents and repairs. On board of a ship these elements were boosted by the omnipresent safety aspect.

The problem of ballast tank corrosion was exacerbated by the introduction of the double hull tanks. In 1989 the Exxon Valdez polluted Prince William Sound and consequently the USA government imposed a new ship design for all tankers carrying oil in US territorial waters, called double hull. IMO followed a few years later and the double hull design became obligatory by the MARPOL convention in 1993 for newly built ships. In contrast with the USA legislation, MARPOL provided the possibility to introduce alternative designs if an equivalent protection was guaranteed by these designs. The purpose of this design was to protect the cargo tanks from damage by providing both primary and secondary containment to increase ship safety and to minimize pollution in case of a calamity (Tator, 2004). Indeed, today, all tankers (and many other vessels as well) have their ballast tanks wrapped around the cargo tanks, serving as a protective barrier. To facilitate tank washing and maintenance, all structural elements were excluded from the cargo tanks and transferred to the ballast tanks, resulting in very unfriendly labyrinth-like structures. On the other hand, all the stiffening elements concentrated in the ballast tanks make them very difficult to access and to be kept shipshape.

Initially, ship owners anticipated corrosion rates to be similar to those encountered in single hulled ballast tanks. Repairs and steel replacement would have to be performed after the third special survey when the ship was 15 years old; however owners of the early double-hulled tankers

found significant corrosion and pitting at the first special survey after only 5 years (Johnson, 2001).

Corrosion in ballast tanks has a complex nature. The corrosion rate is, amongst others, determined by high temperature in the tanks due to the thermos effect, high humidity, the chlorides present in seawater, the cyclic variations wet/dry and cold/warm, high oxygen reduction potential of the seawater, microbial induced corrosion, flexibility of the structures, use of high tensile steel qualities (Germanischer Lloyds, 2000), pollution of the ballast water, marine fouling, galvanic effects, steel qualities. Each and every of these elements has been examined extensively in controlled conditions and the exact individual impact of all of these contributing parameters is well known.

It is extremely complex to model the interaction between this cocktail of elements and therefore a different appreciation can be obtained starting from in situ observations. Once the total corrosion rate has been established an attempt can be made to determine the most critical factor and at this point the established patterns are most useful again.

The protection of ballast tanks is just as complex as the corrosion problem itself. The access is difficult and the environment is unfriendly. The light is scarce and large parts are hard to reach. The cost of decent maintenance is towering high, mainly because the working conditions are troublesome.

The condition of the ballast tanks is determining the economic lifetime of a ship (Lloyds Register, 2006). A ship is brought to the scrap yard when the condition of the ballast tanks becomes unacceptable since restoring is not feasible.

A lot of laboratory work is already done and describes the corrosion process under controlled circumstances. Research starting from reality can give new insights in the corrosion process and might reveal elements and influences that do not show under lab conditions.

This knowledge will enable us to develop new monitoring techniques, to improve planned maintenance and to enhance the security of ship and crew. A better design will avoid important future expenses and improve the cost-effectiveness of the ship. The owners must recognize this need for utmost quality, and understand that the additional money spent up-front for a better coating system will extend the service life of the coating and will be more economical over the long run (Tator, 2004).

2. Principles of corrosion

2 Principles of corrosion

2.1 Key equations

2.1.1. Thermo chemistry

$$E_k = \frac{mv^2}{2}$$

Kinetic energy

$$\Delta E = E_{final} - E_{initial}$$

Change in internal energy

$$\Delta E = q + w$$

Relates the change in internal energy to heat (q) and work (w) (1st law of thermodynamics)

$$w = -P\Delta V$$

The work done by an expanding gas constant pressure

$$\Delta H = \Delta E + P\Delta V$$

Enthalpy change at constant pressure

$$q = C_s \times m \times \Delta T$$

Heat gained or lost based on specific heat (C_s), mass and temperature change

$$\Delta H^0(\text{reaction}) = \Delta H^0(\text{products}) - \Delta H^0(\text{reactants})$$

Standard enthalpy change of a reaction

2.1.2. Chemical thermodynamics

$$\Delta S = \frac{q_{rev}}{T} \text{ (constant T)}$$

Relating entropy change to the heat absorbed or released in a reversible process

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} > 0$$

The 2nd law of thermodynamics

$$S = k \ln W$$

Boltzmann formula, relating entropy to the number of microstates

$$\Delta S^0 = \sum nS^0(\text{products}) - \sum mS^0(\text{reactants})$$

Calculating the standard entropy change from standard molar entropies

$$\Delta S_{surr} = \frac{-\Delta H_{sys}}{T}$$

The entropy change of the surroundings for a process at constant temperature and pressure

$$\Delta G = \Delta H - T\Delta S$$

Calculating change in Gibbs free energy from enthalpy and entropy changes at constant temperature

$$\Delta G^0 = \sum n\Delta G_f^0(\text{products}) - \sum m\Delta G_f^0(\text{reactants})$$

Calculating the standard free energy from standard free energies of formation

$$\Delta G = -w_{\max}$$

Relating the free energy change to the maximum work a process can perform

$$\Delta G = \Delta G^0 + RT \ln Q$$

Equation of Nernst, calculating free energy change under non-standard conditions

$$\Delta G^0 = -RT \ln K$$

Relating the standard free energy change and the equilibrium constant K

2.2 Definition

The question on the nature and rationale behind the formation of rust on metal surfaces was already posed in the cradle of the natural sciences – the city-states of pre-Christian Greece. In his *Timaeus* (59c), Plato⁸ defined rust as the earthy component separating out of the metal. The Renaissance natural philosopher Georgius Agricola⁹ shared the same opinion some 2000 years later in his great mineralogical work *De natura fossilium*: "Iron rust (Lat. ferrugo or rubigo) is, so to speak, a secretion of metallic iron" (Von Baeckman, 1997).

In modern terms, corrosion is the chemical or electrochemical reaction between a material, usually a metal, and its environment that produces a deterioration of the material and its properties (Koch, 2002). Chemical corrosion is the outcome of a direct reaction between the elements and is not the result of substitution or displacement of one element for or by another. This type only occurs at very high temperatures and is not relevant in the context of this paper. Electrochemical/mechanical corrosion may be induced by the presence of tensile stress in the material causing stress corrosion. In the continuation of this chapter, however, we will discuss electrochemical corrosion, also called low temperature corrosion or wet corrosion.

It is a misconception that corrosion is always negative. Sometimes corrosion is a desirable phenomenon. Examples are the passivation layer on top of stainless steel or the etching process during metallographic testing.

2.3 Basic principle

Metals occur in nature most commonly as oxide or sulphide ores in which they are in a higher oxidation state than that of the free metal. Extraction of the metal from its ore involves reduction¹⁰ of the oxidized form to the meta-stable free metal form (figure 25), resulting in an increase in internal free energy. Consequently, the metal will try to lose its excess energy by becoming oxidized¹¹ again, through loss of electrons. This oxidizing tendency of a metal is the driving force for corrosion and it is

⁸ Plato: 428 BC – 348 BC. Classical Greek philosopher, mathematician, writer of philosophical dialogues, and founder of the Academy in Athens.

⁹ Georgius Agricola: 24 March 1494 – 21 November 1555, a German scholar and scientist. Known as "the father of mineralogy".

¹⁰ Reduction: A chemical reaction in which an atom or ion gains electrons from another atom or ion.

¹¹ Oxidation: A chemical reaction in which an atom or ion loses electrons to another atom or ion.

found in virtually all metals except the very noble metals such as gold or platinum (Bogaerts, 1995).

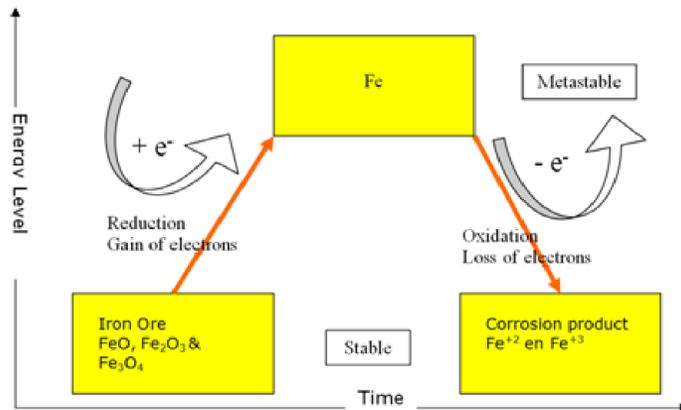


Figure 25: Corrosion is the return of the metal to its natural condition (Mattson, 1996)

2.4 Electrochemical corrosion

2.4.1 Basic concept of electrochemical corrosion

Electrochemical corrosion or wet corrosion requires the presence of 4 elements the presence of

- an anode¹²
- a cathode¹³
- a metallic connection between anode and cathode
- an electrolyte¹⁴.

These 4 elements together make a corrosion cell. The corrosion process in a corrosion cell consists out of an anodic and a cathodic half cell reaction. In the anodic reaction, the metal atoms will be oxidized to metal ions. These ions will dissolve in the electrolyte while the electrons remain behind in the metal, thus creating a negative charge. This makes the process at the anode a destructive one. The metal dissolves and weakens while the cathode remains intact. The surplus of electrons will flow to the cathode through the metallic connection between either electrode. In the cathodic reaction, the electrons will be consumed in the reduction reaction

¹² The *anode* of a device is the terminal where current flows in from outside. (ACID = Anode current into device) (electrons are leaving the anodes through the metallic path and flow towards the cathode)

¹³ The *cathode* of a device is the terminal where current flows out (CCD = Cathode current departs)

¹⁴ Electrolyte: An electrolyte is any substance containing free ions that make the substance electrically conductive

of one of the components of the electrolyte. In a neutral watery solution the dissolved oxygen (O_2) will be reduced to hydroxide anions (OH^-).

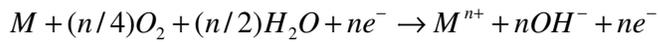
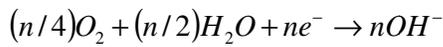
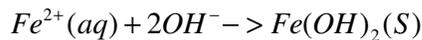


Figure 26 shows a droplet of water on an iron surface as a corrosion cell. The water acts as the electrolyte. The anode is situated in the centre of the water bubble. The iron (Fe) is oxidized to $Fe^{2+} + 2e^-$. The Fe ions go into solution and the electrons move to the edge droplets through the metallic iron.

The outside border of the water droplet becomes cathodic. H_2O , oxygen and the free electrons join to produce hydroxide anions (OH^-).

Within the droplet the hydroxide ions combine with the Fe^{2+} ions. Iron(II) hydroxide precipitates.



Rust is then quickly produced by the oxidation of the precipitate.

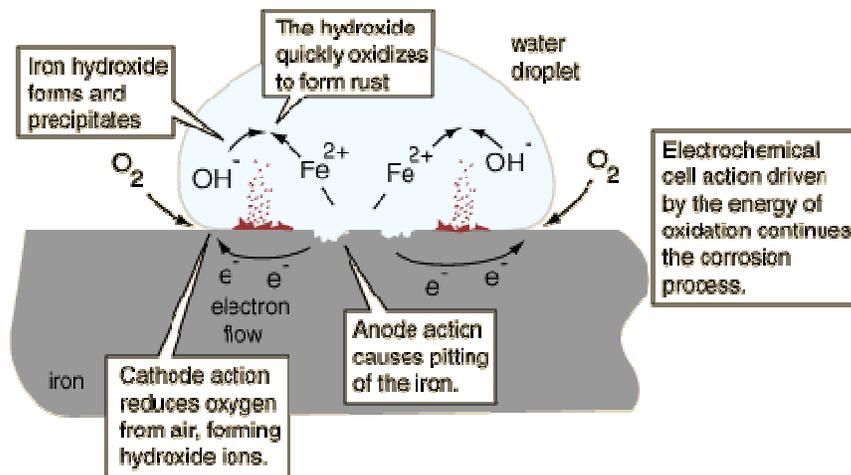


Figure 26: Corrosion cell at the surface of an iron object (Nave, 2005)

The cathode is the driving force behind the process. If the consumption of electrons at the cathode stops, the negative charge of the anode increases which halts the transition of the positive metal ions into the electrolyte, and therefore the entire corrosion process. Moreover, if a negative charge is impressed on the cathode the initial flow of electrons (corrosion current) ceases, and a new flow (a protective current) starts, going from the sacrificial anode to the steel plate being protected. This principle is applied during the cathodic protection of metals by means of sacrificial anodes (as shown in figure 27) or when using an impressed current system.

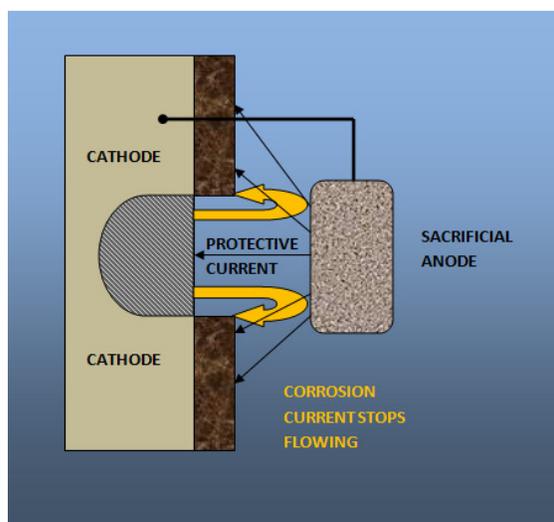


Figure 27: Cathodic protection (own work)

2.4.2 Reduction potentials E

Reduction potential¹⁵ (E , measured in mV) is a measure of the tendency of a chemical element to acquire electrons and thereby be reduced. Each element has its own intrinsic reduction potential. The more positive the potential, the greater the affinity for electrons and the proclivity to be reduced.

Absolute potentials are difficult to measure. Therefore, all reduction potentials are defined in relation to a reference electrode, the standard hydrogen electrode (SHE). The SHE itself has been assigned an arbitrary half cell potential of 0.0 mV. For laboratory use however, the SHE is too fragile to be practical. Other reference electrodes such as Ag/AgCl or saturated calomel (SCE) are commonly used. Moreover, reduction potentials are being measured under standard conditions (where the

¹⁵ Reduction potential also known as redox potential, oxidation/reduction potential or ORP is a measure of the tendency of a chemical species to acquire electrons and thereby be reduced

temperature is set at 25°C, 1 mol/dm³ concentration for each ion participating in the reaction, gas pressures of 1 atmosphere and all the metals are in their pure state). As such, the standard reduction potential at 25°C, E_{298}^0 is obtained. Reduction potentials in non-standard conditions at 25°C are expressed by following equation.

$$E_{298} = E_{298}^0 - \frac{RT}{nF} \ln Q \text{ (The Nernst equation, see 2.5.4)}$$

For iron, the relation between E_{298} and E_{298}^0 can be expressed as follows:



$$E_{298} = E_{298}^0 + \frac{RT}{nF} \ln \left[\frac{[Fe^{2+}]}{[1]} \right]$$

Standard potentials of some electrode reactions at 25°C			
Reduction potentials E^0 pure metals		Stand. potentials E^0 reduction reactions	
$K^+ + e^- \rightarrow K$	-2,92 V	$S + 2 e^- \rightarrow S^{2-}$	-0,48 V
$Ca^{2+} + 2 e^- \rightarrow Ca$	-2,87 V	$Cr^{3+} + e^- \rightarrow Cr^{2+}$	-0,41 V
$Na^+ + e^- \rightarrow Na$	-2,71 V	$2 H^+ + 2 e^- \rightarrow H_2$	0,000 V
$Mg^{2+} + 2 e^- \rightarrow Mg$	-2,34 V	$Cu^{2+} + e^- \rightarrow Cu^+$	+0,153 V
$Al^{3+} + 3 e^- \rightarrow Al$	-1,67 V	$O_2 + 2 H_2O + 4 e^- \rightarrow 4 OH^-$	+0,401 V
$Ti^{2+} + 2 e^- \rightarrow Ti$	-1,63 V	$I_2 + 2 e^- \rightarrow 2 I^-$	+0,53 V
$Zn^{2+} + 2 e^- \rightarrow Zn$	-0,76 V	$O_2 + 2 H^+ + 2 e^- \rightarrow 2 H_2O_2$	+0,69 V
$Cr^{3+} + 3 e^- \rightarrow Cr$	-0,71 V	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0,771 V
$Fe^{2+} + 2 e^- \rightarrow Fe$	-0,44 V	$Br_2 + 2 e^- \rightarrow 2 Br^-$	+1,06 V
$Cd^{2+} + 2 e^- \rightarrow Cd$	-0,40 V	$O_2 + 4 H^+ + 4 e^- \rightarrow 2 H_2O$	+1,230 V
$Ni^{2+} + 2 e^- \rightarrow Ni$	-0,25 V	$Cl_2 + 2 e^- \rightarrow 2 Cl^-$	+1,360 V
$Sn^{2+} + 2 e^- \rightarrow Sn$	-0,14 V	$H_2O_2 + 2 H^+ + 2 e^- \rightarrow 2 H_2O$	+1,77 V
$Pb^{2+} + 2 e^- \rightarrow Pb$	-0,13 V	$F_2 + 2 e^- \rightarrow 2 F^-$	+2,85 V
$2 H^+ + 2 e^- \rightarrow H_2$	0,000 V		
$Cu^{2+} + 2 e^- \rightarrow Cu$	+0,34 V		
$Ag^+ + e^- \rightarrow Ag$	+0,80 V		
$Hg^{2+} + 2 e^- \rightarrow Hg$	+0,85 V		
$Pd^{2+} + 2 e^- \rightarrow Pd$	+0,99 V		
$Pt^{2+} + 2 e^- \rightarrow Pt$	+1,20 V		
$Au^+ + e^- \rightarrow Au$	+1,68 V		

Figure 28: Standard potentials of some pure metals and redox reactions (Smet, 2009)

2.5 Thermodynamics

Thermodynamics¹⁶ studies the state of energy of materials. The extraction of metal out of ore requires a lot of energy to change the energy status from low and stable to high and unstable (figure 25). Sooner or later the metal will return to a thermodynamically stable condition through corrosion. In view of this cycle, corrosion has been described by Fontana as "extractive metallurgy in reverse" (Fontana, 1986).

A corrosion process can be predicted by thermodynamics. To estimate the rate of corrosion, however, one needs kinetics (see 5.2.9).

2.5.1 First law of thermodynamics

When energy is exchanged between the system and the surroundings, it is exchanged as either heat (Q) or Work (w);

$$\Delta E = Q + w$$

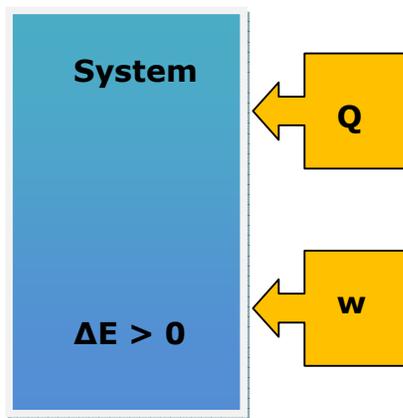


Figure 29: Changes in internal energy (own work)

Sign convention:

ΔE + means gain of energy by system - means loss of energy by system

Q + systems gains heat - system loses heat

w + work done on system - work done by system

The first law of thermodynamics states that a process can transform energy and/or move energy, but cannot create or eliminate it.

¹⁶ Thermodynamics covers the part of physics that deals with the relationships and conversions between heat and other forms of energy.

Figure 30 illustrates that the energy of the universe is a constant. To study thermodynamic problems we need to isolate a certain portion of the universe (the system) from the remainder of the universe (the surroundings).

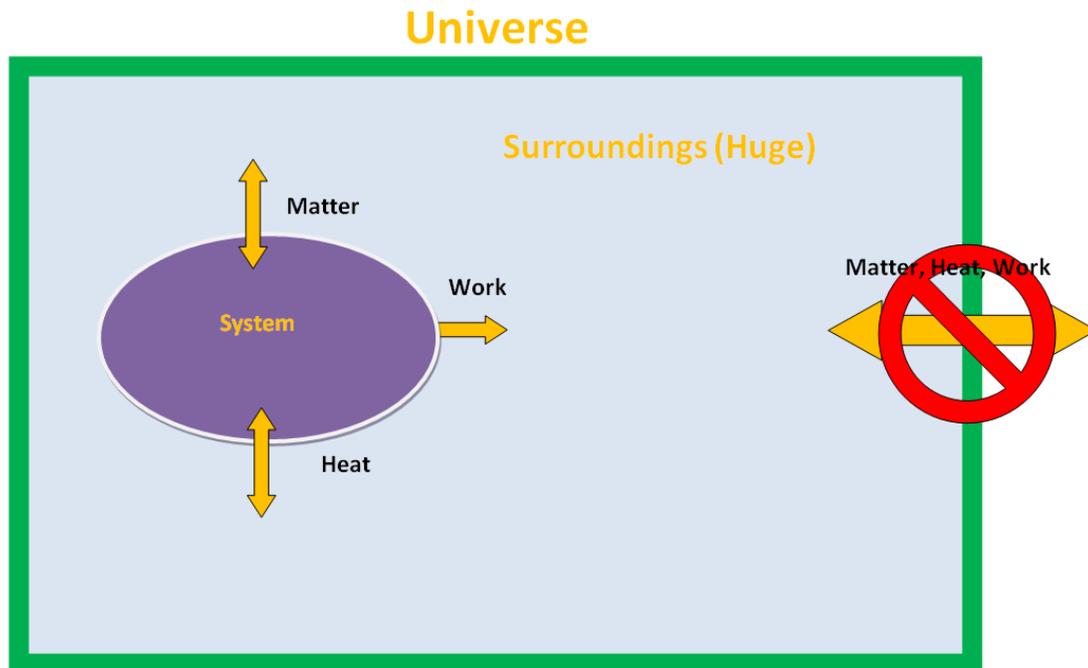


Figure 30: The quantity of energy in the universe is constant (own work)

$$\Delta E_{univ} = 0$$

$$\Delta E_{univ} = \Delta E_{sys} + \Delta E_{sur} = 0$$

$$\Delta E_{sys} = -\Delta E_{sur}$$

In thermodynamics we use the state function enthalpy [H] to represent the heat flow during an isobaric process (Brown, 2009).

The word enthalpy comes from the Greek "heat inside".

The internal energy of a systems is function of the heat added or lost by the system minus the work (w) done by or on the system.

$$w = PV$$

$$E = H - PV \text{ (see figure 30)}$$

$$H = E + PV$$

At constant pressure

$$\Delta H = \Delta(E + PV)$$

$$\Delta H = \Delta E + P\Delta V$$

Since $\Delta E = Q + w$ and $w = -P\Delta V$

$$\Delta H = Q + w - w$$

At constant pressure the change in enthalpy equals the heat gained or lost.

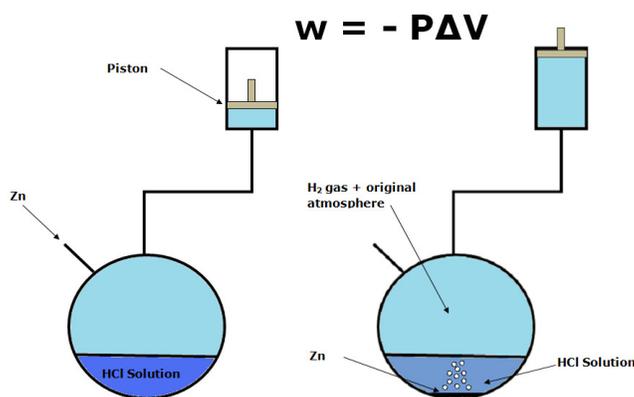


Figure 31: Work done by a system at constant pressure (own work)

For most reactions the difference between ΔH and ΔE is small since $P\Delta V$ is small.

$$\Delta H_{sys} = -\Delta H_{sur}$$

2.5.2 Second law of thermodynamics

As stated before, the first law of thermodynamics tells us that energy can be transferred between a system and the surroundings but the total energy remains constant.

The first law of thermodynamics gives no information regarding the spontaneity of reaction. A spontaneous reaction is one that proceeds on its own without any outside assistance.

When looking for a criterion for spontaneity the second law of thermodynamics and the concept "entropy" needs to be considered.

The second law of thermodynamics is commonly known as the law of increased entropy. In its primeval form, it was put forward by Sadi

Carnot¹⁷, who is considered to be the father of thermodynamics. Carnot observed that it is impossible to convert the energy content of a fuel completely to work because a significant amount of heat is always lost to the surroundings and that work could only be gained from heat by a transfer from a warmer to a colder body.

40 years later, Clausius¹⁸ extended the work of Carnot by attributing a special significance to the ratio of the heat delivered to an ideal engine and the temperature at which it is delivered, Q/T . He called this ratio "entropy" (Brown, 2009).

$$S = \frac{Q}{T} \text{ and } \Delta S = \frac{\Delta Q}{T}$$

According to Clausius, entropy was the amount of thermal energy not available to do work (opposite of energy). In a closed system, available energy can never increase, so its opposite, entropy, can never decrease.

"Entropy" is defined as a measure of unusable energy within a closed or isolated system (the universe for example). As usable energy decreases and unusable energy increases, "entropy" increases. Entropy is also a gauge of randomness or chaos within a closed system. As usable energy is irretrievably lost, disorganization, randomness and chaos increase.

In nature disorder is more common (easier to obtain) than order, so nature tends from order to disorder in isolated systems from low entropy to high entropy.

2.5.3 Josiah Willard Gibbs¹⁹ and the concept of free energy

As S stands for the amount of energy unavailable to do work, another quantity should be introduced to measure the amount that will perform work. To this end, J.W. Gibbs came up in 1873 with the concept of Gibbs free energy (G). This is the energy associated with a chemical reaction that can be used to do work. The Gibbs free energy of a system is its enthalpy (H) minus the product of the temperature and the entropy (S) of the system:

$$G = H - TS$$

$$G = \text{Gibbs Free Energy}$$

¹⁷ Nicolas Léonard Sadi Carnot: 1 June 1796 – 24 August 1832 was a French physicist and military engineer.

¹⁸ Rudolf Julius Emanuel Clausius: Born Rudolf Gottlieb, 2 January 1822 – 24 August 1888, was a German physicist and mathematician.

¹⁹ Josiah Willard Gibbs: February 11, 1839 – April 28, 1903 was an American theoretical physicist, chemist and mathematician.

$$H = \text{Enthalpy} = E + PV$$

(where E = internal energy, P = pressure, V = volume, and T = temperature in Kelvin)

Every chemical reaction, occurring at constant temperature, results in a change in Gibbs free energy which we can measure as

$$\Delta G = (G_{\text{products}} - G_{\text{reactants}}) = (H_{\text{products}} - H_{\text{reactants}}) - T(S_{\text{products}} - S_{\text{reactants}})$$

$$\Delta G = \Delta H - T\Delta S$$

If $\Delta H < 0$, the reaction is exothermic and heat is dissipated. In case of a $\Delta H > 0$ the reaction is endothermic. A reaction will have $\Delta S < 0$ if the reaction results in increased order and $\Delta S > 0$ if the reaction results in increased disorder (entropy).

The net direction of a chemical reaction will be from higher to lower energy. In other words, if the Gibbs free energy of the reactants is higher than the energy of the products, $G_{\text{reactants}} > G_{\text{products}}$, the reaction will occur spontaneously. In such a case, $\Delta G < 0$, and the Gibbs free energy of the system decreases with the reaction. In the opposite case, $\Delta G > 0$, and energy is required for the reaction to occur.

The sign of ΔG depends on the sign of ΔH and ΔS as well as on the value of T.

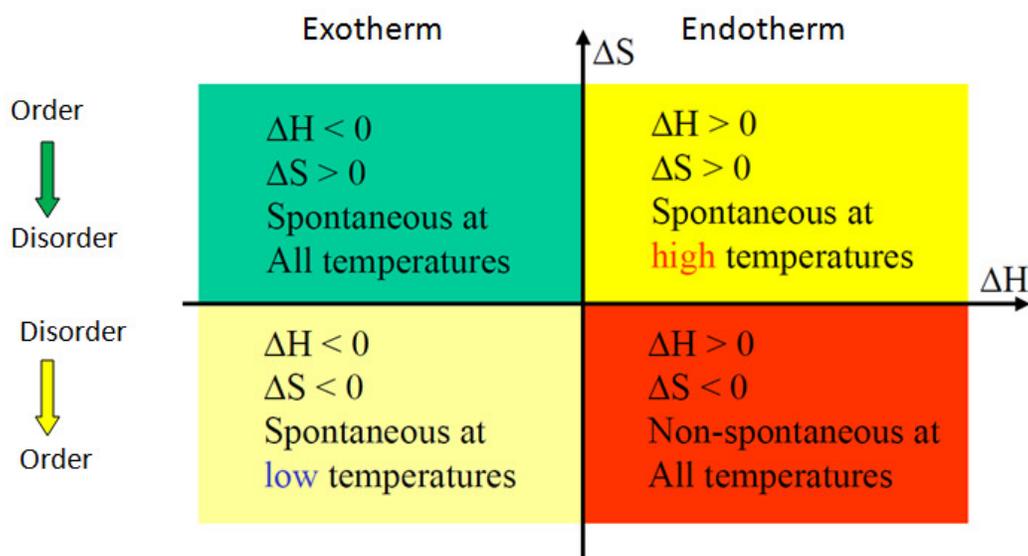


Figure 32A: The spontaneity of electrochemical reactions

The magnitude of ΔG is also significant. ΔG equals the maximum useful work that can be done by a system on its surroundings in a spontaneous process occurring at constant temperature and pressure. It is the portion of the energy change of a spontaneous reaction that is free to do useful work. The remainder of the energy enters the environment as heat.

Figure 32B illustrates that during a reaction the amount of free energy decreases until the reaction is at equilibrium.

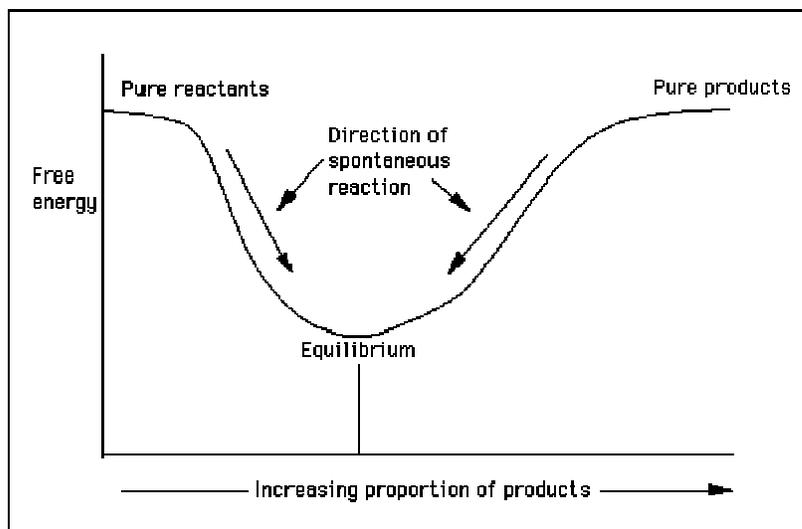


Figure 32B: The spontaneity of electrochemical reactions (UNC, 2008)

2.5.4 Thermodynamics of electrochemistry: the Nernst²⁰ equation

The principles of thermodynamics were introduced into the field of electrochemistry by W.H. Nernst. Electrochemical reactions are basically chemical reactions; their thermodynamics depend on the concentrations of the species involved, as well as on the temperature. The Nernst equation describes this dependence.

To comprehend this transition, let us consider the following. Work is done by an electric field if the electric force acting on a charge causes it to move from one point to another. These two points differ in their electric potential. The magnitude of the work done on the charge by the electric field is $q\Delta V$ where q is the electrical charge and ΔV is the difference in potential. In electrochemistry the difference in reduction potential E is used instead of ΔV .

²⁰ Walther Hermann Nernst (25 June 1864 – 18 November 1941) was a German physical chemist and physicist who is known for his theories behind the calculation of chemical affinity as embodied in the third law of thermodynamics, for which he won the 1920 Nobel Prize in chemistry.

Electrochemically produced work is inextricably a decrease in free energy, and therefore:

$$w = -\Delta G \text{ (or } \Delta G = -w)$$

$$\Delta G = -qE$$

A positive value of E and a negative value of ΔG both indicate that a reaction is spontaneous.

$$q = nF$$

Where n is the number of moles of electrons transferred in a redox reaction, and F the Faraday constant being the total electric charge of a mole of electrons, $F = 96,487 \text{ C/mol}$.

$$\Delta G = -nFE$$

When reactants and products are all in their standard states and at 25°C the previous equation can be written as follows:

$$\Delta G_{298}^0 = -nFE_{298}^0$$

This equation is very important because it relates the standard reduction potential to the standard free energy change.

The Nernst equation allows us to calculate the electric potential of a redox reaction in "non-standard" situations.

Starting point is a general chemical reaction



(The uppercase letters indicate the reactants and their concentrations, while the lowercase letters are the stoichiometric²¹ coefficients for the reaction).

Q = reaction quotient, is a function of the activities or concentrations of the chemical species involved in a chemical reaction. In the special case that the reaction is at equilibrium the reaction quotient is equal to the equilibrium constant K.

Q = Concentration of the products/concentration of the reactants

²¹ Stoichiometry: is a branch of chemistry that deals with calculating the relation between the amounts of substances that take part in a balanced chemical reaction or that combine to form a chemical compound.

$$Q = \frac{C^c D^d}{A^a B^b}$$

Q>K: Reaction favours reactants and shifts right.

Q<K: Reaction favours products and shifts left.

Q=K: No side favoured. No shift. In equilibrium. Q=1 => lnQ =0

$$E_{298} = E_{298}^0 - \left(\frac{RT}{nF} \right) \ln Q$$

E_{298}^0 is the standard potential in volts at 298K (25°C)

$$R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}$$

The equation of Nernst can also be converted into:

$$E_{298} = E_{298}^0 - \left[\frac{8.314510 \text{ JK}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}{n \times 96,485 \text{ C/mol}} \right] 2.303 \log Q$$

$$E_{298} = E_{298}^0 - \left[\frac{0.059}{n} \right] \log Q$$

For more complex systems, however, where a metal or alloy is in contact with a corrosive environment which contains a lot of different anions and cations (e.g. sea water) the electrode potential is not very well defined thermodynamically. Nevertheless, an electrode potential does exist and can be measured. This potential can thus be used to predict the tendency for corrosion to occur (Bogaerts, 2008). The more negative the potential, the more anodic is the metal and the greater is the driving force for corrosion. The more positive the potential, the more noble is the metal or alloy and the more cathodic is its behaviour. A tabulation of some different metals and alloys, according to their corrosion tendency in sea-water, is given in the next figure (Bogaerts, 1995).

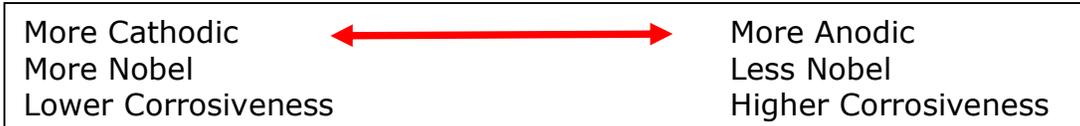
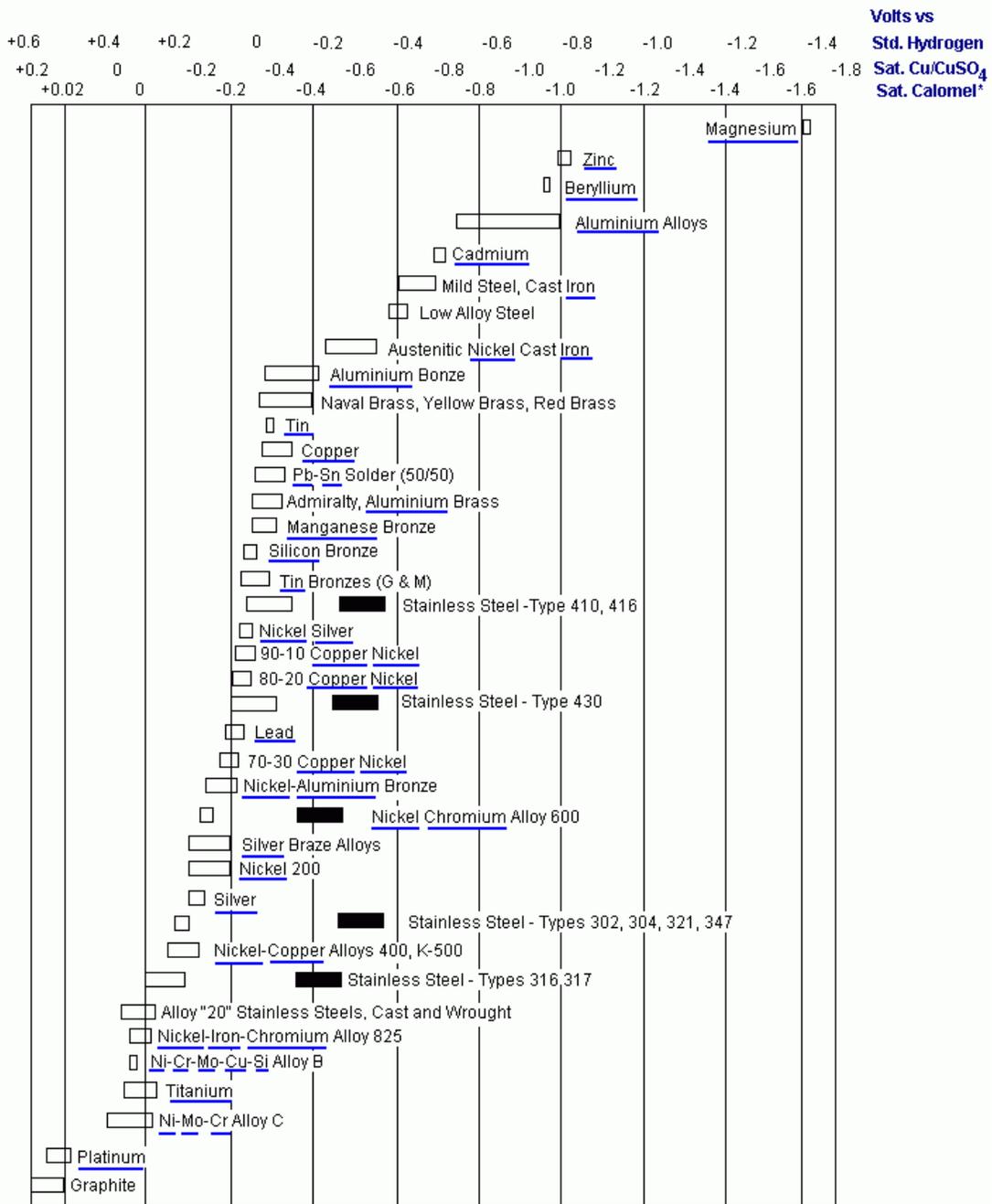


Figure 33: Galvanic series of the most common metals in seawater of 20°C (ASTM, 2009)

2.5.5 Pourbaix²² diagrams or E-pH diagrams

In what follows we will put more emphasis on the chemical behaviour of iron, the major constituent of steel and therefore the most important component in ballast tank corrosion processes.

When iron is brought into an aqueous solution many stable oxidation states may exist, depending on the specific conditions.

1. $2e^- + 2H^+ = H_2$
2. $4e^- + O_2 + 4H^+ = 2H_2O$
3. $2e^- + Fe(OH)_2 + 2H^+ = Fe + 2H_2O$
4. $2e^- + Fe^{2+} = Fe$
5. $2e^- + Fe(OH)_3 + 3H^+ = Fe + 3H_2O$
6. $e^- + Fe(OH)_3 + H^+ = Fe(OH)_2 + H_2O$
7. $e^- + Fe(OH)_3 + 3H^+ = Fe^{2+} + 3H_2O$
8. $Fe(OH)_3^- + H^+ = Fe(OH)_2 + H_2O$
9. $e^- + Fe(OH)_3 = Fe(OH)_3^-$
10. $Fe^{3+} + 3H_2O = Fe(OH)_3 + 3H^+$
11. $Fe^{2+} + 2H_2O = Fe(OH)_2 + 2H^+$
12. $e^- + Fe^{3+} = Fe^{2+}$
13. $Fe^{2+} + H_2O = FeOH^+ + H^+$
14. $FeOH^+ + H_2O = Fe(OH)_{2(s\ln)} + H^+$
15. $Fe(OH)_{2(s\ln)} + H_2O = Fe(OH)_3^- + H^+$
16. $Fe^{3+} + H_2O = FeOH^{2+} + H^+$
17. $Fe(OH)^{2+} + H_2O = Fe(OH)_2^+ + H^+$
18. $Fe(OH)_2^+ + H_2O = Fe(OH)_{3(s\ln)} + H^+$
19. $FeOH^{2+} + H^+ = Fe^{2+} + H_2O$
20. $e^- + Fe(OH)_2^+ + 2H^+ = Fe^{2+} + 2H_2O$
21. $e^- + Fe(OH)_{3(s\ln)} + H^+ = Fe(OH)_{2(s\ln)} + H_2O$
22. $e^- + Fe(OH)_{3(s\ln)} + 2H^+ = FeOH^+ + 2H_2O$
23. $e^- + Fe(OH)_{3(s\ln)} + 3H^+ = Fe^{2+} + 3H_2O$

Table 1: Stable oxidation states of iron in an aqueous solution (Madou, 2004)

With the use of thermodynamic theory (in particular the Nernst equation), Pourbaix diagrams can be constructed. These diagrams show the thermodynamic stability of species as a function of potential E and pH.

²² Marcel Pourbaix: 1904-1998, chemist, born in Russia, studied in Brussels and graduated from the Faculty of Applied Sciences of the Université Libre de Bruxelles in 1927.

Such diagrams can provide valuable information in the study of corrosion phenomena (Madou, 2004).

E-pH or Pourbaix diagrams show regions or fields where dissolved species and precipitates are stable (Pourbaix, 1974). Most of the time the stable oxidation states of a metal are represented on top of the stability diagram for water.

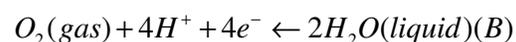
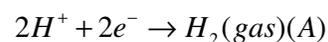
Water is thermodynamically stable between the two black lines as shown on figure 34. Above the superior line O₂ is evolved and beneath the lower line H₂ is developed.

When a metal is exposed to an aqueous solution, the conditions are as a rule, equivalent to a point between these 2 lines.

Stability diagram of water

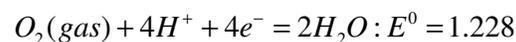
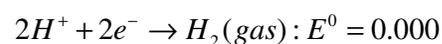
For the construction of a Pourbaix diagram the two parameters E en pH are plotted for the various equilibria on normal Cartesian coordinates with E as ordinate and pH as abscissa.

Water in aqueous form can only exist between the potential required to oxidize water and the potential to reduce water.



We simplify by setting the temperature at 25°C and supposing an O₂ (gas) and H₂ (gas) pressure of 1 atm.

Standard reduction potential (E⁰) of the half-reactions



$$E = E^0 - (0.059/n) \log\left(\frac{[C]^c [D]^d}{[A]^a [B]^b}\right)$$

$$E = E^0 - (0.059/n) \log(\text{concentration products} / \text{concentration reactants})$$

$$E_A = E_{H^+/H_2}^0 - (0.059/2) \log(PH_2 / [H^+]^2)$$

$$(PH_2 = 1atm)$$

$$(pH = -\log[H^+])$$

$$E_A = 0.000 - (0.059/2)\log[PH_2] + (0.059/2)2\log[H^+]$$

$$E_A = 0.000 - (0.059/2)\log 1 - 0.059pH$$

$$E_A = 0.000 - 0.059pH$$

$$E_B = E_{O_2/H_2O}^0 - (0.059/4)\log\left(\frac{[H_2O]^2}{[H^+]^4 PO_2}\right)$$

$$E_B = 1.228 - (0.059/4)\log(1/[H^+]^4)$$

$$E_B = 1.228 - (0.059/4)4pH$$

$$E_B = 1.228 - 0.059pH$$

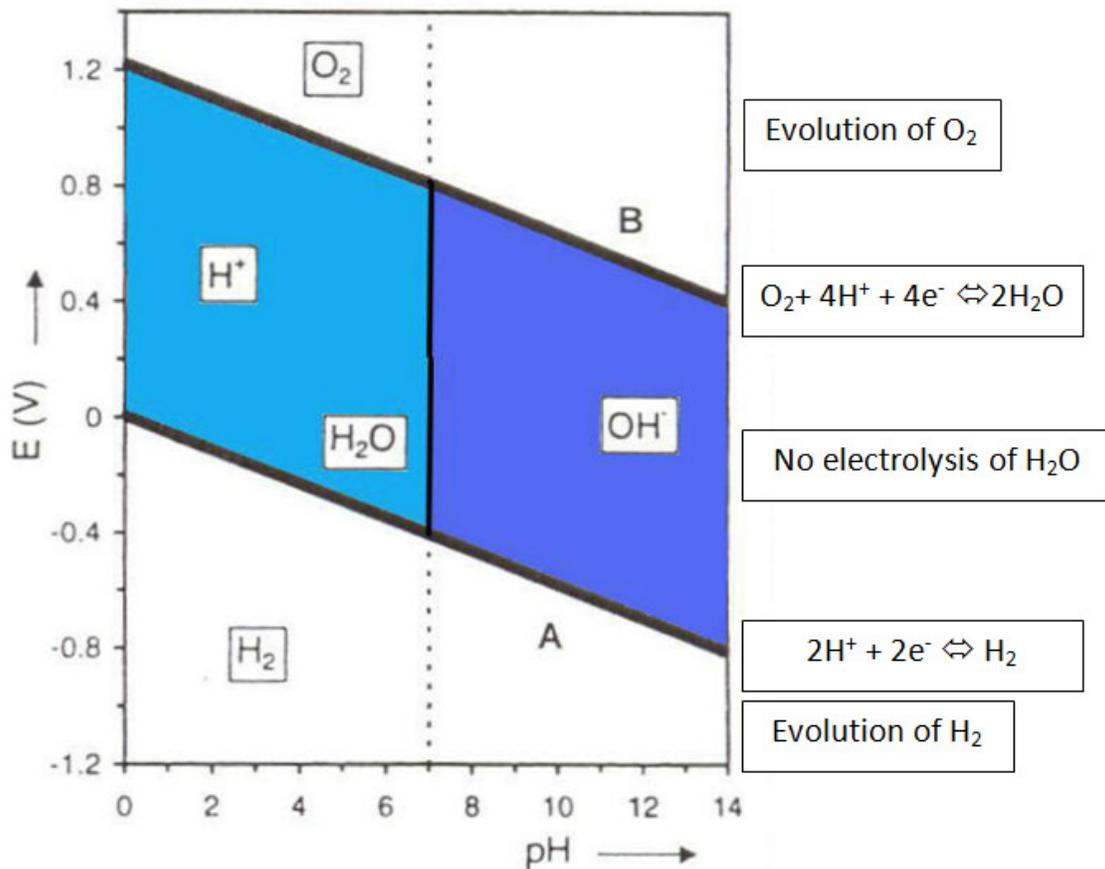


Figure 34: Simplified Pourbaix diagram water (Smet, 2008)

2.5.6 Pourbaix diagram of Fe (Bogaerts, 1995)

The full diagram for iron is quite complex, since many equilibria are involved. Fortunately a useful simplified diagram can be obtained considering following equilibria:

- (I) $Fe \leftrightarrow Fe^{++} + 2e^{-}$
- (II) $Fe^{++} \leftrightarrow Fe^{+++} + e^{-}$
- (III) $Fe^{++} + 3OH^{-} \leftrightarrow Fe(OH)_3 + e^{-}$
- (IV) $Fe^{+++} + 3H_2O \leftrightarrow Fe(OH)_3 + 3H^{+}$
- (V) $Fe + 3H_2O \leftrightarrow Fe(OH)_3 + 3H^{+} + 3e^{-}$
- (VI) $Fe + 2H_2O \leftrightarrow FeO_2H^{-} + 3H^{+} + 2e^{-}$
- (VII) $FeO_2H^{-} + H_2O \leftrightarrow Fe(OH)_3 + e^{-}$

E(V)

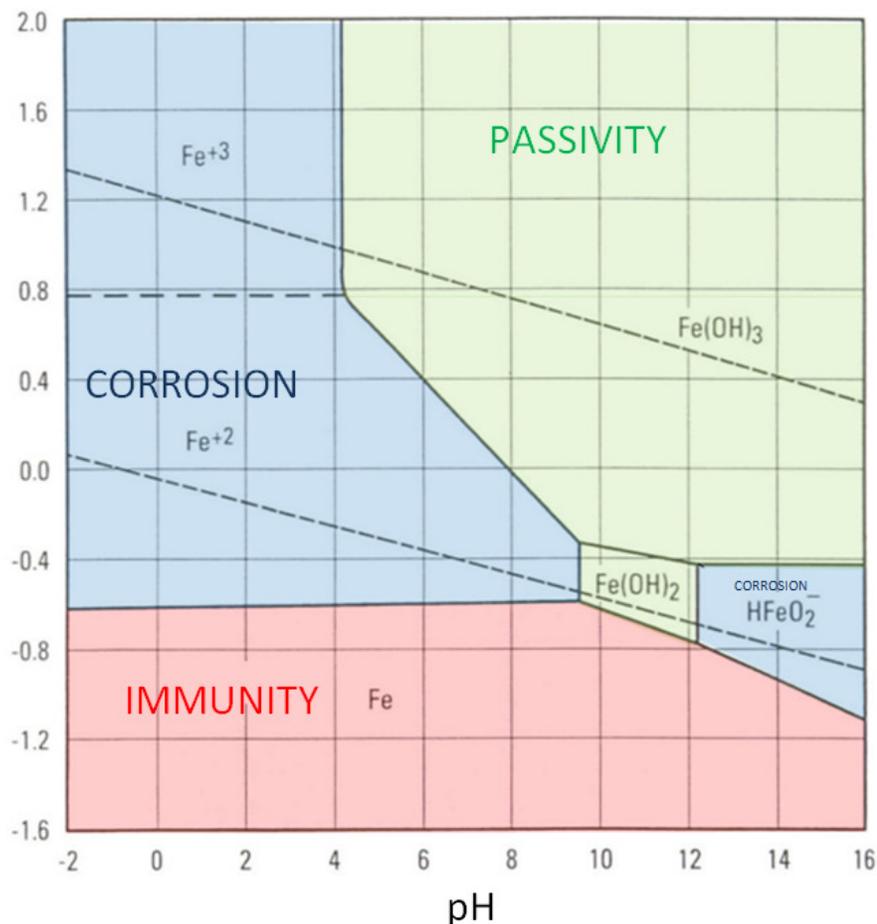


Figure 35: Simplified corrosion diagram of iron in water 25°C (Bogaerts, 1995)

A simplified Pourbaix diagram indicates regions of "Immunity", "Corrosion" and "Passivity", instead of the stable species. They thus give a guide to the stability of a particular metal in a specific environment. Immunity means that the metal is not attacked, while corrosion shows that general attack will occur. Passivation occurs when the metal forms a stable coating of an oxide or hydroxide on its surface. The best example is the relative stability of aluminium because of the alumina layer formed on its surface when exposed to air.

For iron this means that the $\text{Fe}(\text{OH})_3$ layer will protect the metal surface if it is impervious and highly adherent.

Other passivating metals are zinc, titanium and silicon.

2.5.7 Advantages/disadvantages of Pourbaix diagrams

The Pourbaix diagrams are a convenient way to visualize thermodynamic principles and to determine the probability of a corrosion reaction to occur under certain conditions of pressure, temperature and chemical environment. The information in the diagrams can be beneficially used to influence corrosion of pure metals in an aqueous environment. By altering the pH and potential to the regions of immunity and passivation, corrosion can be controlled.

However, there are several limitations of these diagrams, which are summarized below:

1. These diagrams are purely based on thermodynamic data and do not provide any information on the reactions. No information is provided on the rates of reaction.
2. Consideration is given only to equilibrium conditions in a specified environment and factors which may seriously affect the corrosion rate, such as temperature and velocity, are not considered.
3. The activity of species is arbitrarily selected as $10^{-6} \text{ gmol}^{-1}$ which is not realistic.
4. Pourbaix diagrams deal with pure metals which are not of much interest to the engineers.
5. All insoluble products are assumed to be protective which is not true, as porosity, thickness, and adherence to substrate are important factors, which control the protective ability of insoluble corrosion products.

Although the above disadvantages appear to be substantial, the advantages offered by the Pourbaix diagrams far outweigh their limitations (Ahmad, 2006).

It can be very misleading to consult only the thermodynamic data concerning a corrosion reaction. The isolated fact that a system has a small thermodynamic potential does not necessarily mean that the corrosion reaction will be slow because in practice the kinetic factors may render the reaction particularly easy (Bogaerts, 1995). When it comes to corrosion, it is particularly interesting to be able to calculate the amount of mass that will be liberated at the anode in function of the time. Naval architects take this loss in account when they determine the thickness of the ship construction elements. A corrosion allowance is provided on top of the minimum required structural dimensions in respect of the strength of the ship.

2.5.8 Faraday's laws of electrolysis

Faraday's law of electrolysis relates a mass of substance liberated with an electrical charge.

First law:

The mass of primary products formed at an electrode by electrolysis is directly proportional to the quantity of electricity.

$$m \approx It \text{ or } m = ZIt$$

Where I = current (in A)

t = time (seconds)

m = mass of the primary product in grams

Z = constant of proportionality (electrochemical equivalent). It is the mass of a substance liberated by 1 ampere-second of a current (1 coulomb).

(Ahmad, 2006)

Second Law:

The masses of different primary products formed by equal amounts of electricity are proportional to the ratio of molar mass to the number of electrons involved with a particular reaction:

$$m_1 \approx \frac{M_1}{n_1} \approx Z_1$$

$$m_2 \approx \frac{M_2}{n_2} \approx Z_2$$

m_1, m_2 = masses of primary product in grams

M_1, M_2 = molar masses (g/mol)

n_1, n_2 = number of electrons

Z_1, Z_2 = electrochemical equivalent.

(Ahmad, 2006)

Combining the first law and the second law:

$$m = Zit \quad (1^{\text{st}} \text{ law})$$

$$Z = k \frac{M}{n} \quad (2^{\text{nd}} \text{ law})$$

$$m = k \frac{M}{n} It$$

$$m = \frac{1}{F} \frac{M}{n} It$$

Where F = Faraday's constant. It is the quantity of electricity required to deposit the ratio of mass to the valence of any substance and expressed in Coulombs per gram equivalent (C/g equivalent) or Coulombs per mol. The Faraday constant, F , is the quantity of electricity carried by one mole of electrons.

F = Faraday constant = 96,485 C/mol

In terms of loss of mass of a metal with time we get:

$$\frac{dm}{dt} = \frac{MI}{nF}$$

We divide both parts of the equation by A , the exposed area of the metal

$$\frac{dm}{Adt} = \frac{MI}{nFA}$$

$I/A = i$ or the current density.

$$\frac{dm}{dt} = \frac{AMi}{nF}$$

Mass = density x loss of thickness x surface

Once the loss of mass has been determined the corrosion depth (d) can be established.

$$\frac{\Delta d}{\Delta t} = \frac{M}{nF\rho} i$$

d = corrosion depth

ρ = mass density

	mA cm ⁻²	mm year ⁻¹	mpy	g m ⁻² day ⁻¹
mA cm ⁻²	1	3.28 M nday ⁻¹	129 M nday ⁻¹	8.95 M n ⁻¹
mm year ⁻¹	0.306 nday M ⁻¹	1	39.4	2.74 day
mpy	0.00777 nday M ⁻¹	0.0254	1	0.0694 day
g m ⁻² day ⁻¹	0.112 nM ⁻¹	0.365/day	14.4/day	1

^ampy = milliinch per year; n = number of electrons freed by the corrosion reaction; M = atomic mass; d = density.

^bNote: The table should be read from left to right, that is, 1 mA cm⁻² = (3.28 M nday⁻¹)mm year⁻¹ = (129 M nday⁻¹) mpy = (8.95 M n⁻¹) g m⁻² day⁻¹.

Table 2: Conversion between current, mass loss and penetration rates for all metals (Roberge, 2007).

	mA cm ⁻²	mm y ⁻¹	mpy	g m ⁻² day ⁻¹
mA cm ⁻²	1	11.6	456	249
mm year ⁻¹	0.0863	1	39.4	21.6
mpyear	0.00219	0.0254	1	0.547
g m ⁻² day ⁻¹	0.00401	0.0463	1.83	1

^aNote: The table should be read from left to right, that is, 1 mA cm⁻² = 11.6 mm year⁻¹ = 456 mpy = 249 g m⁻² day⁻¹.

Table 3: Conversion between current, mass loss and penetration rates for steel (Roberge, 2007).

2.5.9 Polarization diagrams of corroding metals: E/i curves and Evans diagrams

Polarization diagrams of corroding metals, sometimes called Evans diagrams, are graphs of potential E versus log current I or log current density i.

They were originally developed by U.R. Evans at the University of Cambridge in England, who recognized the usefulness of such diagrams for predicting corrosion behaviour (Uhlig, 2008).

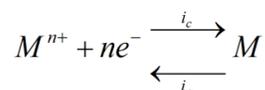
Following Faraday's law of electrolysis the speed of dissolution can be rated by an electric current I.

I_{corr} cannot be measured directly by means of a simple ammeter. Polarization is used and the changes in potential of an electrode caused by changes in the current flowing through it (or vice versa) are measured.

The measurements are usually made using a potentiostat, an instrument that automatically maintains the desired potential between working and reference electrodes by passing the appropriate current between the working and the counter electrode.

The working electrode potential (E) is deviated from an equilibrium (E_{eq}) position due to the passage of an electrical current. This electrochemical phenomenon is called polarization.

The electrode reaction of a metal can be written as follows:



Conventionally the cathodic current I_{cathode} or I_c is negative and the anodic current I_{anode} or I_a is positive.

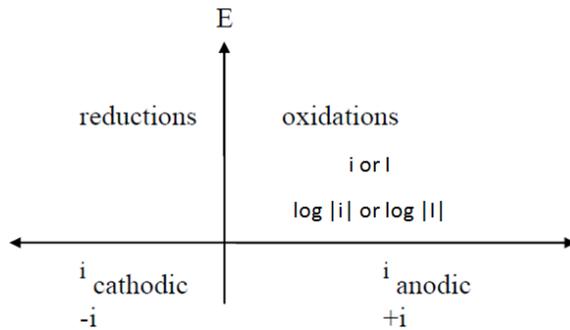
When the cell is balanced $|I_c| = |I_a|$ or $I_c + I_a = 0$, the net current is 0 and no electrons will be exchanged. No mass will be added or removed at cathode or anode.

A single electrode is balanced when the potential E equals the equilibrium potential E_{eq} . Otherwise, the electrode is polarized²³, and the difference $\eta = E - E_{\text{eq}}$ is defined as the overpotential η . A positive η causes a net anodic current while a negative overpotential causes a net cathodic current.

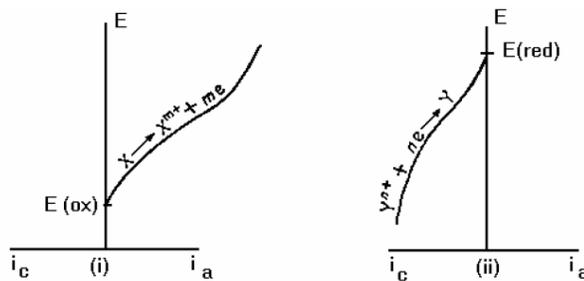
²³ Polarization: The change of potential of an electrode from its equilibrium potential upon the application of a current.

If E represents the potential at which a reaction is taking place on an electrode, then the kinetic data can be plotted on axes having E as ordinate and I or i as abscissa. i is the current density corresponding with the current I per surface unit.

$+i$ or i_a are anodic current densities and $-i$ or i_c cathodic current densities



36 A: Coordinate system of E/i curves



36 B: Some typical E/i curves

Figure 36: Coordinate system of the E/i curves and some typical E/I curves (Bogaerts & Zheng, 1995)

The horizontal axis is placed at some arbitrary potential. Often a semi-logarithmic plot is used: E vs. $\log |I|$ (or $\log |i|$) (see figure 36A&B).

When the corrosion cell is balanced, $I_a + I_c = 0$. At that moment the cell reduction potential = E_{corr} .

The anodic reactions and the cathodic reactions in a system cannot be measured and studied individually.

If an E/i curve is plotted on the basis of i being the net current density as measured with an external ammeter as a function of a varying potential E, then both reactions, reduction as well as oxidation, will be included in the measurement without discrimination, to provide an apparent curve. This curve will cross the vertical at E_{corr} at which the net apparent current is zero. Such a curve is often called an apparent polarization curve and sometimes an electrolysis curve (Bogaerts, 1995).

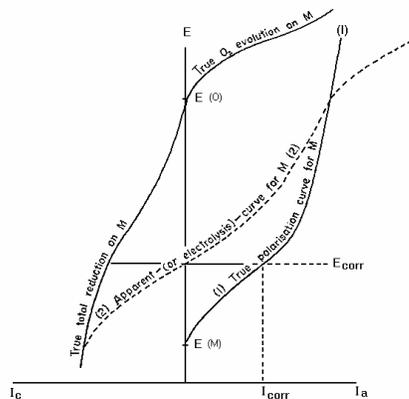


Figure 37: True and apparent polarization curves for a metal M (Bogaerts & Zheng, 1995)

If the curves for the anodic and cathodic reactions are plotted as potential (E) vs. logarithm of the current density, with the - sign of the cathodic curve neglected and if the true values are replaced by an approximate line the term Evans²⁴ diagram is used.

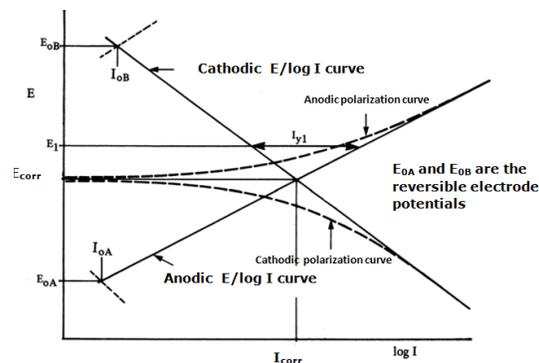


Figure 38: Evans diagram and Tafel lines as determined with a potentiostat (Bardal, 2004)

²⁴ Ulick Richardson Evans: 1889-1980, laid the foundations of the electrochemical nature of corrosion. His 1937 book *Metallic Corrosion, Passivity, and Protection* is probably the most comprehensive book ever written by a single author on corrosion science.

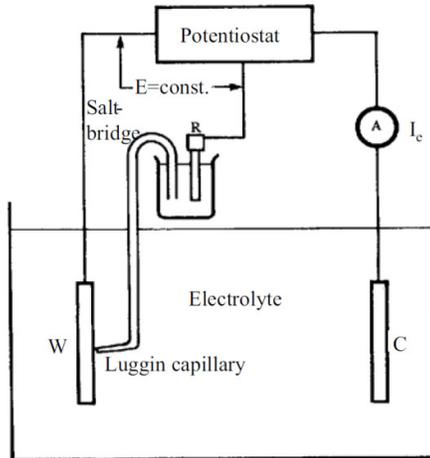


Figure 39: Potentiostat (Bardal, 2004)

W= Working electrode

R = Reference electrode

C = Counter electrode

The potentiostat keeps the electrode potential constant at a set value, by delivering the necessary current between the counter electrode and the working electrode.

We assume that there are two possible electrode reactions on the working electrode, with $E/\log|I|$ curves and corrosion potential E_{corr} as shown by the solid curves in figure 38.

E_{corr} is measured between the working electrode and the reference electrode with no current flowing (open circuit).

When $E = E_{\text{corr}}$ no external current is supplied to the working electrode. If, by means of the potentiostat, we set another arbitrary potential E_1 , an external current I_{y1} is supplied, which is the difference between the anodic and the cathodic reaction current at this potential. If we draw the logarithm of the external current as a function of potential, we obtain the dotted curves shown in the figure. These curves are called polarization curves.

It is seen that the $E/\log|I|$ are asymptotes to the polarization curves. When E deviates much from the corrosion potential, the polarization curves and the over-voltage curves merge, and this fact is utilized.

In figure 38 we started with the $E/\log|I|$ curves and drew the polarization curves on this basis. But the purpose is to determine the $E/\log|I|$ curves from the polarization curves, i.e. to go the opposite way.

We record I_{y1} as a function of potential by means of the potentiostat, i.e. we record the polarization curves. The linear part of the polarization curves is extrapolated, and thus the $E/\log|I|$ curves are determined (Bardal, 2004).

I_{corr} is determined by the intersection of the anodic and cathodic $E/\log|I|$ curves.

Figure 40 shows the polarization lines (solid line) of a metal M in an acid solution. In this figure, E_r = reversible potential, the equilibrium potential at the anode or the cathode, and $E_{r, M^{n+}/M}$ = the reversible potential at the corroding metal. At this potential the rate of dissolution equals the rate of deposition.

Since the conditions are deviating from the standard conditions the equation of Nernst is used to determine E_r .

$$E_{r, M^{n+}/M} = E^0_{M^{n+}/M} + \frac{RT}{nF} \ln a_{M^{n+}}$$

In general the potential of the metal does not reach the reversible potential since the electrons are consumed by alternative reactions. In an acid solution the H^+ ions are soliciting to produce hydrogen gas²⁵. $2H^+$ (absorbed on the metal surface) + $2e^-$ (in the metal) $\rightarrow H_2$ (gas).

The consumption of the electrons triggers a number (determined by the valence number) of metal ions to go into solution leading to corrosion.

At the cathode also a reversible potential $E_{r, H^+/H_2}$ can be calculated using the equation of Nernst.

$$E_{r, H^+/H_2} = E^0_{H^+/H_2} + \frac{RT}{F} \ln \frac{P_{H_2}^{1/2}}{a_{H^+}}$$

Corrosion can now proceed at a potential E_{corr} such that the rate of the anodic reaction of metal dissolution is equal at the rate of cathodic

²⁵ In a neutral solution the electrons will react with free oxygen and water molecules to produce hydroxide ions. ($O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$)

reactions of hydrogen and /or oxygen reduction. The generated current is I_{corr} , the generated current density is i_{corr} .

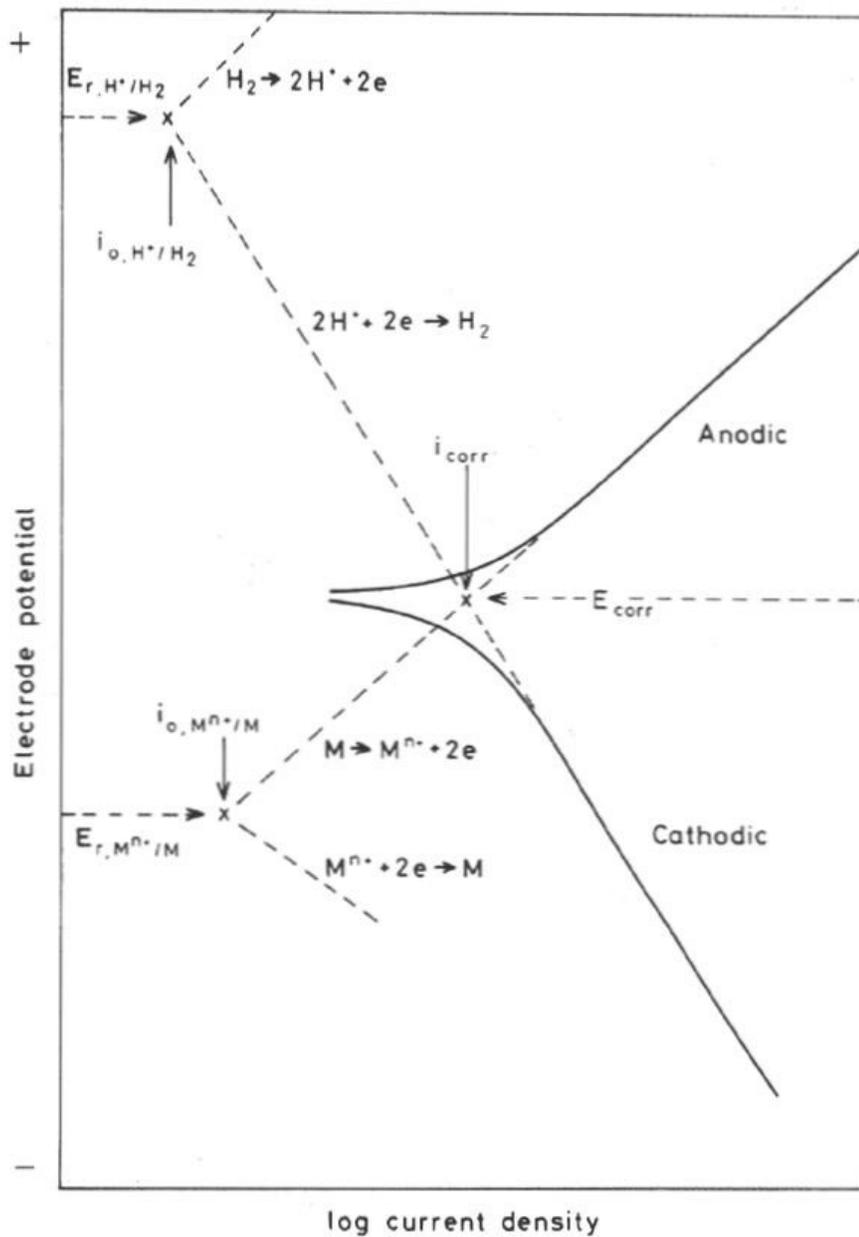


Figure 40: Evans diagram. Schematic anodic and cathodic polarization curves (solid lines) for a metal corroding in an acid solution (Thomas, 2007)

2.5.10 Polarization kinetics

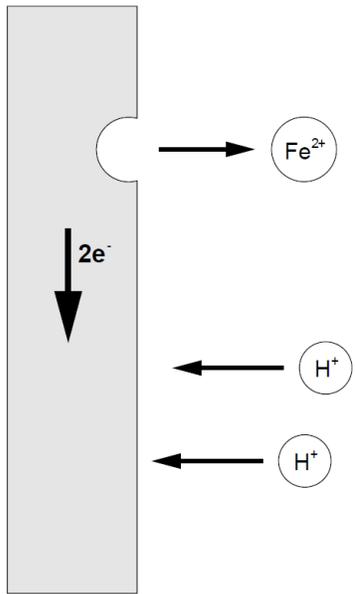


Figure 41: Simple model describing the electrochemical nature of corrosion processes (Roberge, 2000)

The figure above shows the chemical reactions at the surface of a single electrode immersed in water.

Metal ions go into solution at anodic areas in an amount chemically equivalent to the reaction at cathodic areas.

At the anode $Fe \rightarrow Fe^{2+} + 2e^{-}$

At the cathode $2H^{+} + 2e^{-} \rightarrow H_2$ in a de-aerated solution or $4H^{+} + O_2 + 4e^{-} \rightarrow 2H_2O$ in the presence of oxygen.

When iron corrodes the rate is usually controlled by the cathodic reaction which in general is much slower than the anodic reaction.

Consequently the potential of the material will no longer be at an equilibrium value. The deviation from the equilibrium value is called polarization and measured in terms of overvoltage with respect to the equilibrium potential E_{eq} .

$\eta = E - E_{eq}$ is the overpotential

$E_{eq} = E_{298}$

The total overpotential η_{total} consists of 3 elements

η_{act} : Activation overpotential (polarization)

η_{conc} : Concentration overpotential (polarization)

iR : Ohmic drop

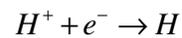
$$\eta_{\text{total}} = \eta_{\text{act}} + \eta_{\text{conc}} + iR$$

Activation polarization

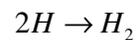
The term activation polarization makes reference to retarding factors that are an inherent part of the kinetics of all electrochemical reactions.

An electrochemical reaction proceeds through several successive steps. The reaction rate is controlled by the slowest step of the process.

A common cause of cathodic activation polarization is hydrogen formation and evolution at the cathode surface. Hereby, hydrogen ions are absorbed from the electrolyte at the surface of the cathode (1). Then, an electron transfer occurs from anode to the hydrogen ions to form hydrogen (2).



Which will then combine with itself to form hydrogen gas molecules (3)



leading to the formation of hydrogen gas bubbles (4).

The slowest of these four steps, dictates how fast the overall reduction reaction happens. Apparently, the limiting step is the transfer of electrons at the surface of the metal (the second step, figure 42).

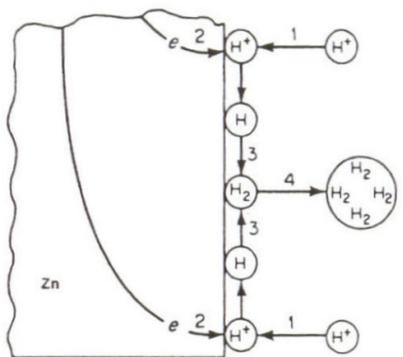


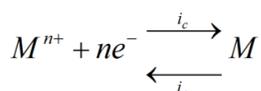
Figure 42: Different steps activation polarization of hydrogen ions (Smet, 2009)

In general all (electrochemical) reactions obey the Arrhenius²⁶ equation:

$$k = A \exp\left[\frac{-E_a}{RT}\right]$$

Wherein k quantifies the speed of a chemical reaction; A is a frequency factor, specific for each reaction and depending on the probability that the molecules will collide in a correct way; E_a is the activation energy, i.e. the energy that must be overcome in order for a chemical reaction to occur. Activation energy may also be defined as the minimum energy required to start a chemical reaction. The activation energy of a reaction is usually denoted by E_a , and given in units of kilojoules per mole. R is universal gas constant, and T is the temperature in Kelvin

For this type of polarization the relation between the net current and the overpotential is laid down by the Butler-Volmer equation.



$$i = i_a + i_c$$

Following Arrhenius the anodic and cathodic current densities are defined by:

$$i_a = i_0 \exp\left[\frac{\alpha n F}{RT} \eta\right]$$

$$i_c = -i_0 \exp\left[\frac{-(1-\alpha)nF}{RT} \eta\right]$$

With α being the transfer coefficient, the fraction of the potential difference at the surface of an electrode that assists charge difference in one direction but discourages it in the other direction, with a value between 0 and 1, frequently being about 1/2. It is related to the slope of a graph of the logarithm of the current against the potential. i_0 the exchange current density. This is the current density when the reaction is going both ways it is when $i_a = i_c$ or $i_a + i_c = 0$.

The total current (I) in a system is the sum of $i_a + i_c$:

²⁶ Svante August Arrhenius (19 February 1859 – 2 October 1927) was a Swedish scientist originally a physicist, but often referred to as a chemist and one of the founders of the science of physical chemistry

$$i = i_0 \left[\exp \left[\frac{\alpha n F}{RT} \eta \right] - \exp \left[\frac{-(1-\alpha) n F}{RT} \eta \right] \right]$$

While the Butler-Volmer equation is valid over the full potential range, simpler approximate solutions can be obtained over more restricted ranges of potential.

- 1) If $|\eta| < 0.01V$ the potential the Butler-Volmer equation can be simplified.

$$R_p = \frac{dE}{di} = \frac{\eta}{di} = \left(\frac{d(E - E_{298})}{di} \right)_{E-E_{298}=0} = \frac{RT}{nFi_0}$$

R_p = Polarization resistance

As η is either positive or negative, becomes larger than about 0.12V, the second or the first term of equation becomes negligible, respectively. Hence, simple exponential relationships between current (i.e., rate) and overpotential are obtained, or the overpotential can be considered as logarithmically dependent on the current density. This theoretical result is in agreement with the experimental findings of the German physical chemist Julius Tafel (1905), and the usual plots of overpotential versus log current density are known as Tafel lines.

- 2) If $|\eta| > 0.12V$ the second term of the Butler-Volmer equation becomes negligible and the equation can be noted as follows:

The anodic Tafel-equation

$$i = i_0 \left[\exp \left[\frac{\alpha n F}{RT} \eta \right] \right] \Rightarrow \ln \frac{i}{i_0} = \frac{\alpha n F}{RT} \eta \Rightarrow \frac{2.3RT}{\alpha n F} \log \frac{i}{i_0} \Rightarrow \eta = \beta_a \log \frac{i}{i_0} \text{ when}$$

$$\beta_a = \frac{2.3RT}{\alpha n F}$$

If $|\eta| < -0.12V$ the first term of the Butler-Volmer equation becomes negligible and the equation can be noted as follows:

The cathodic Tafel-equation

$$i = i_0 \left[-\exp \left[\frac{-(1-\alpha) n F}{RT} \eta \right] \right] \Rightarrow \eta = \beta_c \log \frac{i}{i_0} \text{ when } \beta_c = \frac{2.3RT}{(1-\alpha) n F}$$

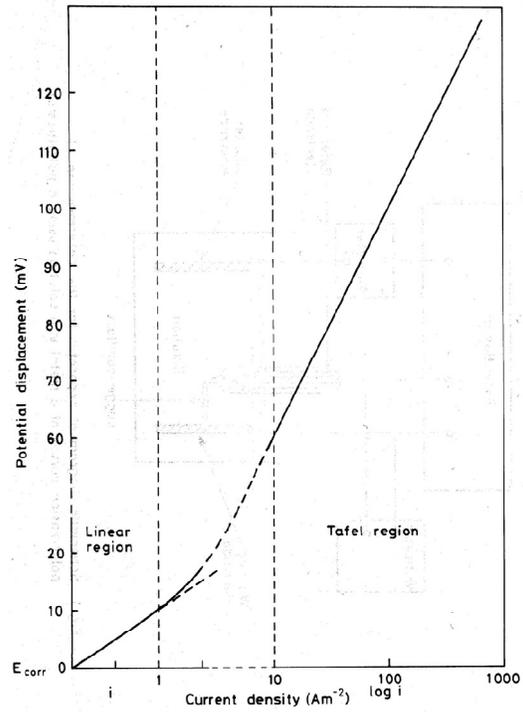


Figure 43: Schematic anodic polarization curve (Thomas, 2007)

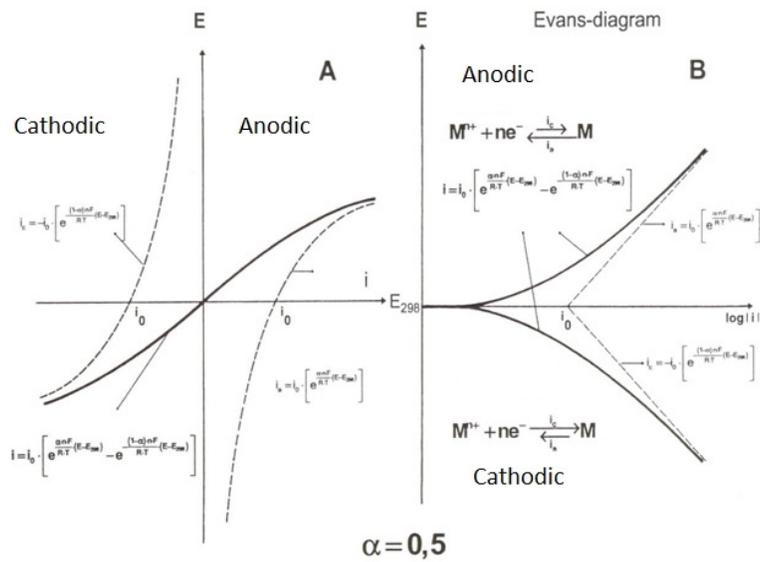


Figure 44: Activation polarization diagrams (Smet, 2009)

Diffusion²⁷ or concentration polarization

Concentration polarization is the polarization component that is caused by concentration changes in the environment adjacent to the surface as illustrated in the following figure. When a chemical species participating in a corrosion process is in short supply, the mass transport of that species to the corroding surface can become rate controlling (Roberge, 2000).

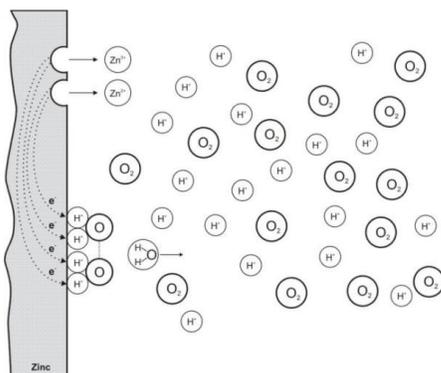


Figure 45: Concentration changes in the vicinity of an electrode causing a concentration polarization effect (Roberge, 2010)

A frequent case of concentration polarization occurs when the cathodic processes depend on the reduction of dissolved oxygen since it is usually in low concentration, i.e. in parts per million (ppm). Tabel 4 contains data related to the solubility of oxygen in air saturated water at different temperatures and data on the solubility of oxygen in seawater of different salinity, chlorinity, and temperatures. In both tables, the level of dissolved oxygen is seen to increase as the temperature decreases.

²⁷ Diffusion is the movement of chemical species (ions or molecules) under the influence of concentration difference. The species will move from the high concentration area to the low concentration area till the concentration is uniform in the whole phase. Diffusion in solutions is the most important phenomenon in electrochemistry. Diffusion also occurs in gases and solids.

Solubility of oxygen in air saturated water

Temperature (°C)	Volume (cm ³)*	Concentration (ppm)	Concentration (M) (μmol L ⁻¹)
0	10.2	14.58	455.5
5	8.9	12.72	397.4
10	7.9	11.29	352.8
15	7.0	10.00	312.6
20	6.4	9.15	285.8
25	5.8	8.29	259.0
30	5.3	7.57	236.7

* cm³ at 0°C per kg of water.

Oxygen dissolved in seawater in equilibrium with a normal atmosphere

Chlorinity* (‰)	0	5	10	15	20
Salinity* (‰)	0	9.06	18.08	27.11	36.11
Temperature(°C)	Ppm				
0	14.58	13.70	12.78	11.89	11.00
5	12.79	12.02	11.24	10.49	9.74
10	11.32	10.66	10.01	9.37	8.72
15	10.16	9.67	9.02	8.46	7.92
20	9.19	8.70	8.21	7.77	7.23
25	8.39	7.93	7.48	7.04	6.57
30	7.67	7.25	6.80	6.41	5.37

* chlorinity refers to the total halogen ion content as titrated by the addition of silver nitrate, expressed in parts per thousand, i.e. ‰.

* salinity refers to the total proportion of salts in sea water, often estimated empirically as chlorinity x 1.80655, also expressed in parts per thousand, i.e. ‰.

Table 4: Solubility of oxygen in seawater (Roberge, 2010)

The layer in which these reactions take place at the metal–solution interface has a thickness in the order of 10 nm.

Several phenomena tend to hinder the movement of ions in the solution (e.g. resistance to the diffusion of oxygen) or delay the oxidation at the anode (or the reduction at the cathode), because the electrode surface has undergone modifications for reasons such as deposition of corrosion products or inhibitors.

A mathematical relation between the overpotential and the polarization current has been established by Nernst based on the 1st law of Fick²⁸:

²⁸Fick's 1st law relates the diffusive flux to the concentration field, by postulating that the flux goes from regions of high concentration to regions of low concentration, with a magnitude that is proportional to the concentration gradient (spatial derivative)

$$\eta = \frac{0.059}{n} \log \left[1 - \frac{i}{i_g} \right]$$

$$i_g = -nFD \left[\frac{C_o}{\delta} \right]$$

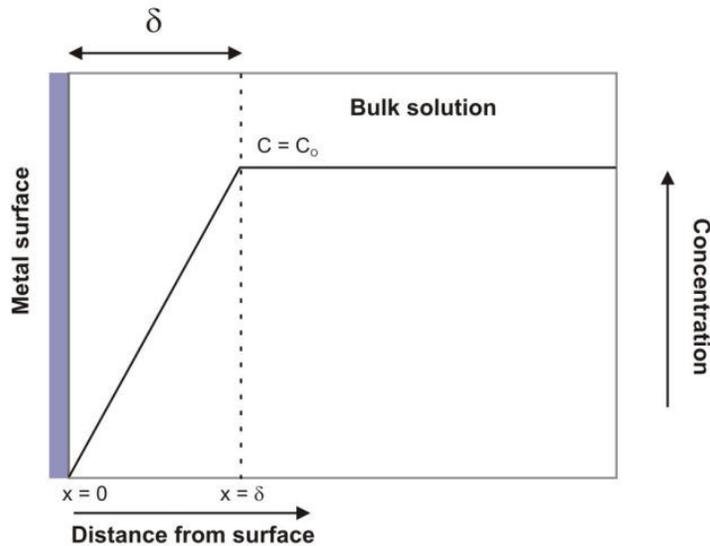


Figure 46: Nernst diffusion layer for a limiting current situation (Roberge, 2010)

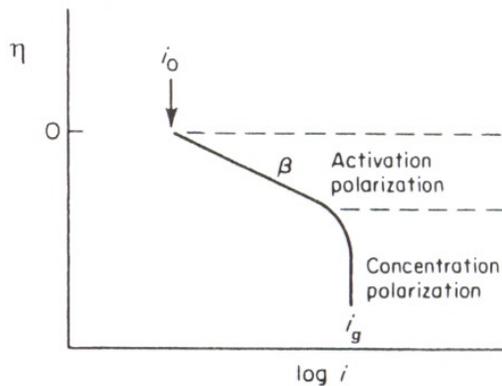


Figure 47: Combined cathodic polarization (Smet, 2009)

When it comes down to corrosion of a metal in an acid solution the current in the cathode is defined by the number of electrons that are consumed by the reduction of hydrogen ions to hydrogen.

Figure 47 depicts the relation between η (overpotential, $E - E_r$) and $\log |i|$.

Initially, when we lower the potential starting from E_r ($\eta = 0$). During β , activation polarization, the speed of the reaction and thus $\log i$ is controlled by slowest "step" in a series of reaction steps.

When the potential is lowered further the concentration polarization region is reached. In this part the speed of the reaction is controlled by the availability of reducible ions at the cathode, the limits of diffusion are reached. Again referring to a metal in an acid solution this means that all of the H^+ ions around the cathode are eaten up by the reaction. Further lowering the potential will not increase $\log|i|$.

i_g increases with temperature, concentration, layer speed and the number of participating electrons and decreases with an increased layer thickness.

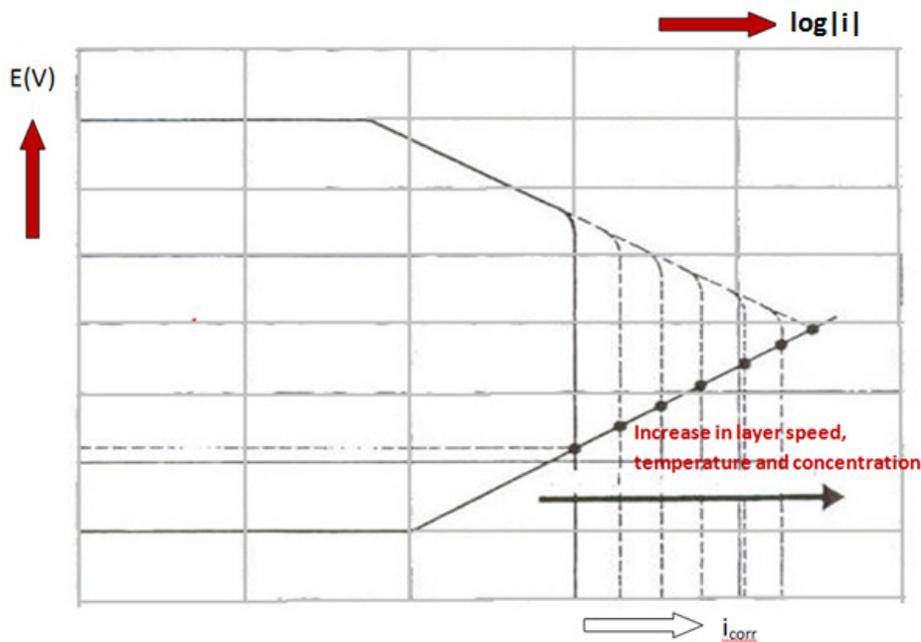


Figure 48: Influence of layer speed, temperature and concentration on the corrosion rate (Smet, 2009)

Ohmic drop

The influence of an anodic or cathodic site on adjacent metals is depending on the conductivity of the environment. For naturally occurring corrosion, the anodic and cathodic sites often are adjacent grains or micro-constituents and the distances involved are very small.

water	$\Omega, \rho.cm$
Pure water	20,000,000
Distilled water	500,000
Rain water	20,000
Tap water	1,000-5,000
River water (brackish)	200
Seawater (coastal)	20
Seawater (open sea)	20-25

Table 5: Ohmic drop (Roberge , 2000)

On the 5th of March 2010, together with J.P. Smet we performed at the Karel De Grote-hogeschool corrosion measurements on a sample of ship construction steel immersed in sea water with a potentiostat. The corrosion rate was determined with the LPR-method²⁹ and the construction of the Tafel lines.

TAFEL CALCULATIONS

Corrosion Rate = 19.64 mpy $\chi^2 = 1.07E+002$
 $E(i=0) = -549.1 \text{ mV}$ $i_{corr} = 42.68 \text{ uA}$
Beta Anodic = $109.2E-3$ Beta Cathodic = $696.0E-3 \text{ V/decade}$
Begin = -753.5 mV End = -331.0 mV

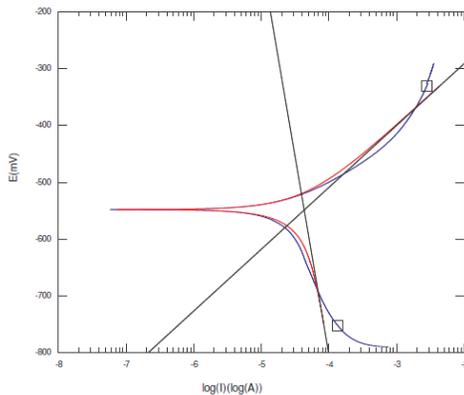


Figure 49: Cathodic diffusion polarization of O₂ (Own work)

²⁹ LPR measures corrosion rate by monitoring the relationship between electrochemical potential and current generated between electrically charged electrodes in a process stream. LPR is most effective in aqueous solutions.

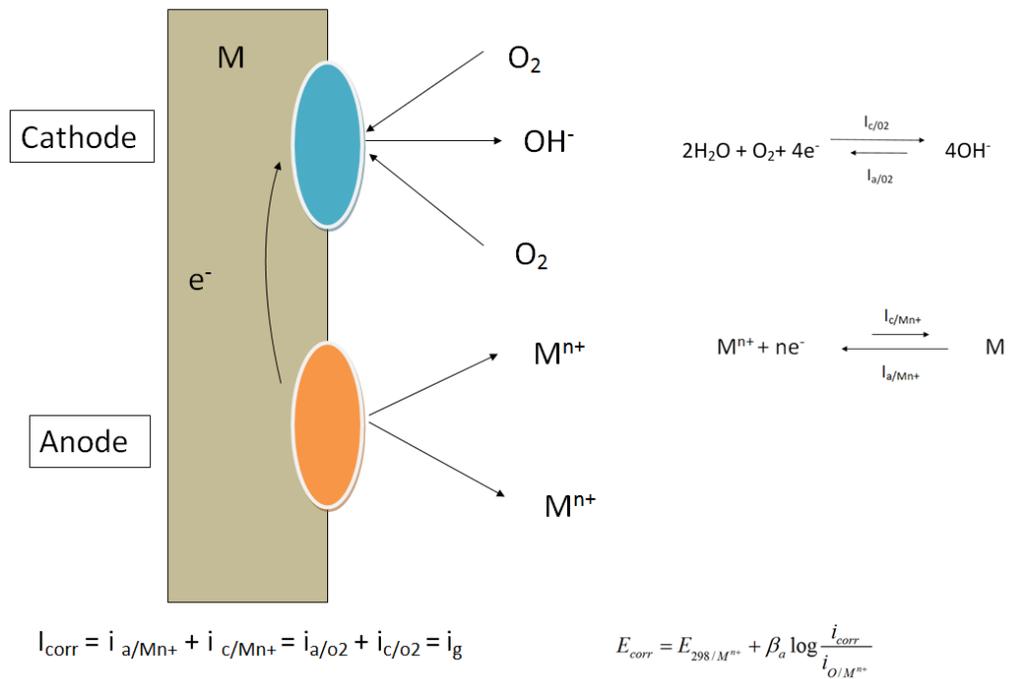


Figure 50: Reaction equations corrosion of a metal in an oxygenous solution (Smet, 2009)

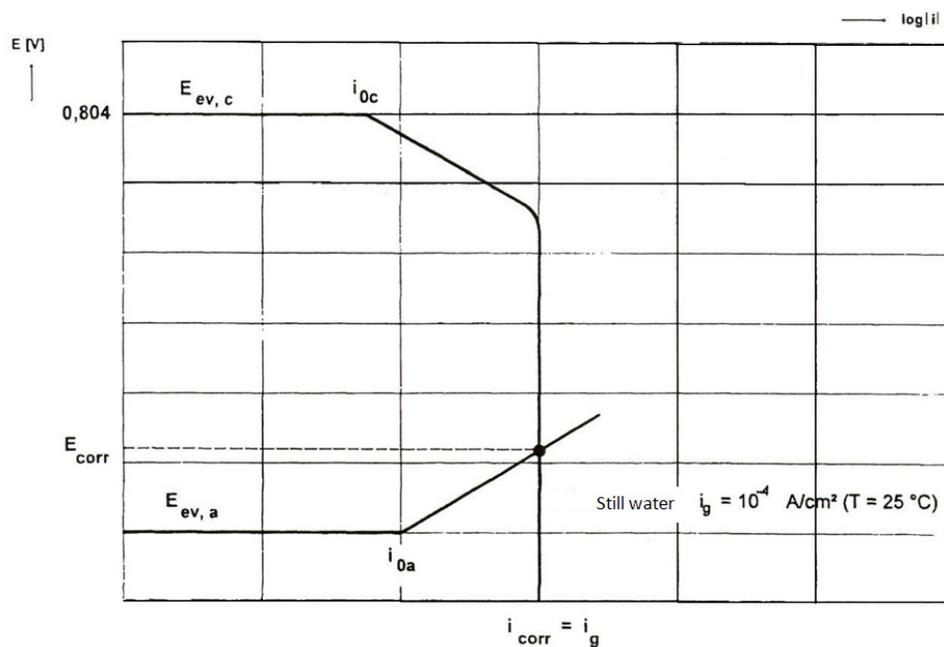


Figure 51: Dual polarization diagram concentration polarization (Smet, 2009)

2.6 Environmental factors influencing the corrosion speed

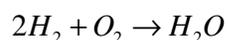
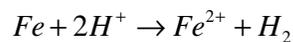
This list of environmental elements influencing the rate of corrosion is not exhaustive. Most of the time more than one element is disturbing the process at same time. In Frank Speller's publication "Corrosion: causes and prevention – An engineering problem" published in 1926 we found the following list and it is still applicable today.

- Hydrogen-ion concentration (pH) in the solution
- Influence of oxygen in solution adjacent to the metal (diffusion)
- Specific nature and concentration of other ions in solution
- Rate of flow of the solution in contact with the metal
- Ability of environment to form a protective deposit on the metal
- Temperature
- Cyclic stress (corrosion fatigue)
- Contact between dissimilar metals or other materials as affecting localized corrosion
- Humidity
- Salinity
- The presence of a coating
- Tensile stress
-

2.6.1 Discussion of the most important elements

Diffusion of oxygen

Oxygen dissolved in water is probably the most troublesome corrosive substance. The product of corrosion of iron by oxygen containing water is a mixture of iron oxides, usually hydrated, and generally referred to as rust. The following equations illustrate this in the simplest form and in water containing only dissolved oxygen.



The action of the oxygen is twofold: it depolarizes the cathode, and it oxidizes the ferrous ions (Fe^{2+}) to ferric ions (Fe^{3+}), which form the insoluble ferric hydroxide ($Fe(OH)_3$). Ferric hydroxide is a brown powder that is insoluble in water.

The stable oxidation states of Fe can be derived from the appropriate Pourbaix or E-pH diagrams (figure 35).

If the formation of ferric hydroxide occurs away from the metal surface, the corrosion product will not be able to stifle the reaction (passivation). In a closed system, this reaction will continue until the dissolved oxygen is used up and the corrosion stops. However, in a system in contact with the air, the oxygen supply is continually replenished. The rate of corrosion, in this case, is generally restricted by the transport of oxygen from the air through the water to the metal (diffusion).

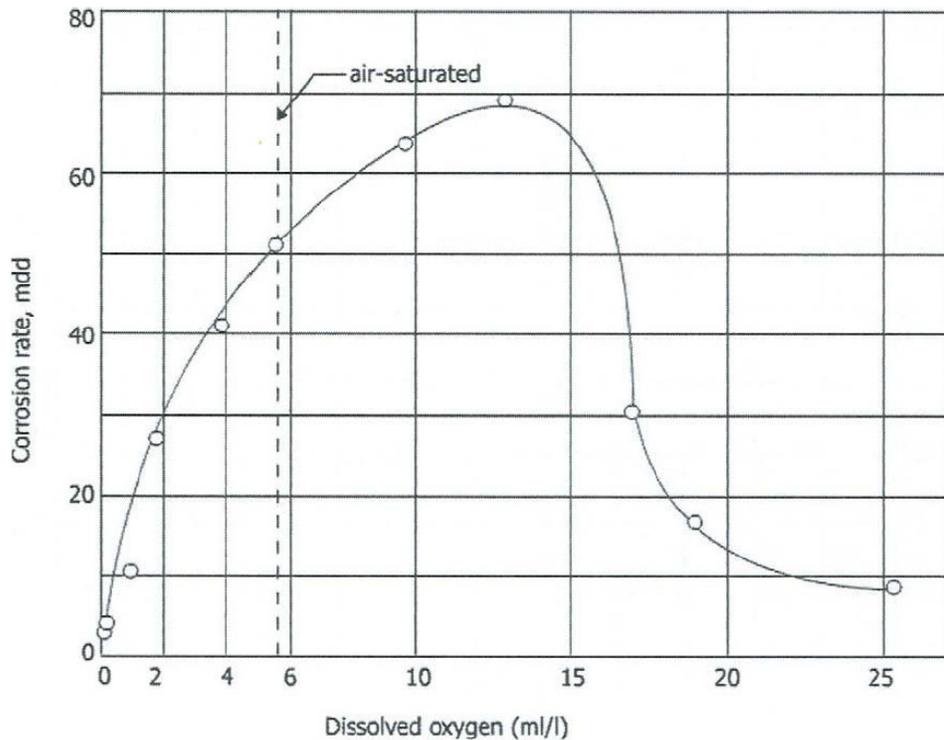


Figure 52: Effects of dissolved oxygen level of corrosion of mild steel in distilled water (25°C, 48 h) (Uhlig, 1995)

The corrosion rate of steel in water has been found to be approximately proportional to oxygen content up to 10 mg/L. At higher oxygen concentrations, the corrosion rate is lower. This may be explained by the fact that at low oxygen concentrations, the corrosion product which is formed initially, hydrated ferrous hydroxide, is not as impermeable to oxygen diffusion as that formed at higher oxygen concentrations. However, at high oxygen concentrations, the ferrous hydroxide is oxidized at a rate which is sufficiently rapid to precipitate the hydrated ferric hydroxide next to the metal as a protective film. In other words, passivation occurs.

The solubility of oxygen in water is also influenced by the concentration NaCl (Gellings, 1997). The explanation is rather simple. Oxygen is soluble in water and oxygen is insoluble in salt. Therefore, the more salt in solution the less oxygen can dissolve per litre of solution.

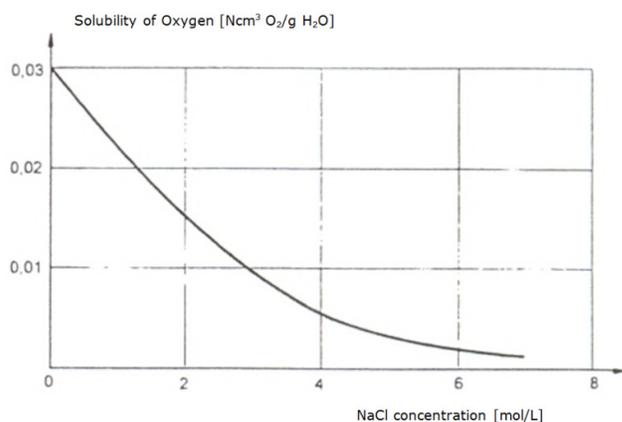


Figure 53: Solubility of oxygen in function of concentration NaCl (Gellings, 1997)

The salt concentration in sea water is approximately 35g/L. (= 3.5% or 599mM or 0.599 Mol/L) At this concentration, the corrosion rate is at its maximum. In waters containing salt concentrations superior to 35g/L the corrosion is proportional to the amount of oxygen dissolved in the water. As the salt concentration in the water increases, the solubility of oxygen decreases and, consequently, the corrosion rate is reduced.

Corrosion can also be caused by differential aeration cells, which are concentration cells caused by differences in oxygen concentration between two parts of the system. This results in a difference in potential between the portion of high oxygen concentration and that of low oxygen concentration, where the corrosion eventually occurs. Corrosion of iron for example, which occurs at a water-air interface, can be attributed to differential aeration. Oxygen from the air is available to water line area. As oxygen is depleted at levels beneath the water line, the area above the waterline becomes cathodic to the immersed iron.

In hard water³⁰, the alkaline cathodic reaction³¹ products, containing calcium and magnesium, precipitate on the iron and shield a part of it from the aerated solution³². Since this shielded area is deprived of oxygen, corrosion occurs here at the water line. (Kok, 2009)

pH and alkalinity

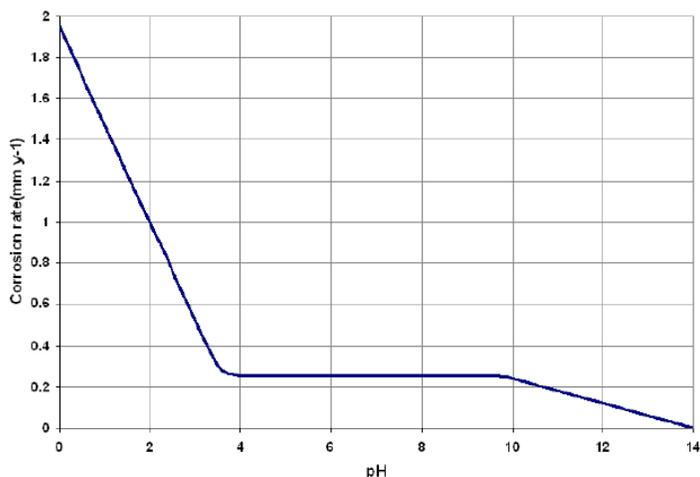


Figure 54: Corrosion rate in function of pH (Roberge, 2010)

In the range of pH 4 to pH 10, the corrosion rate of iron is relatively independent of the pH of the solution and is governed largely by the rate at which oxygen reacts with absorbed atomic hydrogen, and hence, with the rate at which the surface is depolarized and the reduction is allowed to continue.

For pH values below 4.0, the corrosion precipitation dissolves as it is formed rather than depositing on the metal surface to form a film. In the absence of the protective oxide film, the metal surface is in direct contact with the acid solution, and the corrosion reaction proceeds at a greater rate than it does at higher pH values.

In acid solutions below a pH of 4, hydrogen production is substantial as well, indicating that the corrosion rate no longer depends entirely on depolarization by oxygen, but on a combination of the two factors (hydrogen evolution and depolarization).

³⁰ Hard water is water that has high mineral content (in contrast with soft water). Hard water minerals primarily consist of calcium (Ca^{2+}), and magnesium (Mg^{2+}) metal cations, and sometimes other dissolved compounds such as bicarbonates and sulfites and sulfates.

³¹ Formation of OH^- at the cathode

³² Corrosion decreases due to passivation in an alkaline environment

For pH values above about pH 10, the corrosion rate is observed to fall even further.

This might be due to an increase in the rate of the reaction of oxygen with $\text{Fe}(\text{OH})_2$ in the oxide layer to form the more protective Fe_2O_3 (U.S. Department of Energy, 1993)

Temperature

Like most other chemical reactions, corrosion rates increase along with the temperature. Temperature and pressure of the medium govern the solubility of the corrosive species in the fluid, such as oxygen (O_2), carbon dioxide (CO_2), chlorides, and hydroxides. For example, as shown in figure 55, the rate of corrosion increases monotonically with increased temperature, however, above 80°C , the corrosion rate tends to drop because of a fall in the level of dissolved oxygen (Amad, 2006).

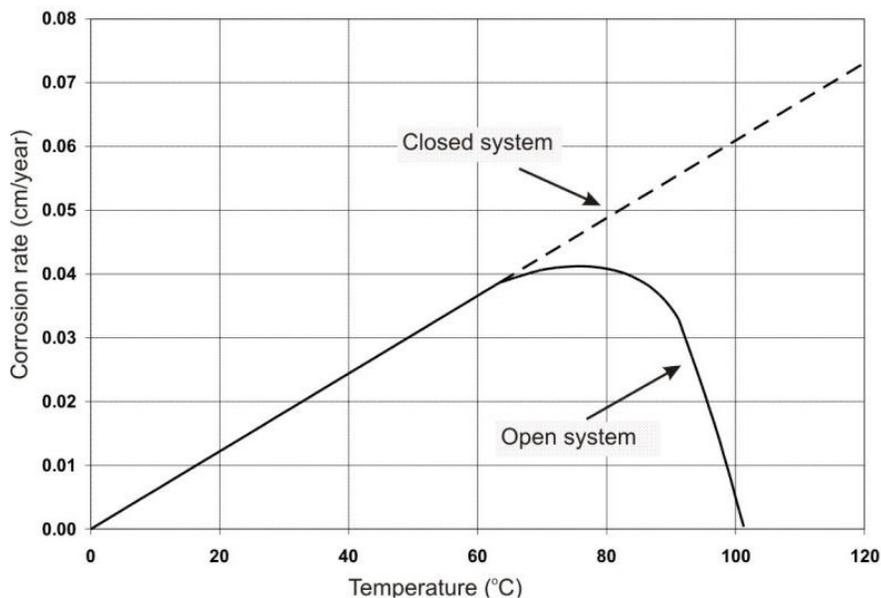


Figure 55: Relative increase of corrosion rate in function of the temperature (RINA, 2004)

Salinity

Seawater typically contains about 3.5% sodium chloride, although the salinity may be weakened in some areas by dilution with fresh water or concentrated by solar evaporation in others. Seawater is normally more corrosive than fresh water because of the higher conductivity and the penetrating power of the chloride ion through surface films on a metal. The rate of corrosion is controlled by the chloride content, oxygen availability, and the temperature. The 3.5% salt content of seawater produces the most corrosive chloride salt. (Roberge, 2010)

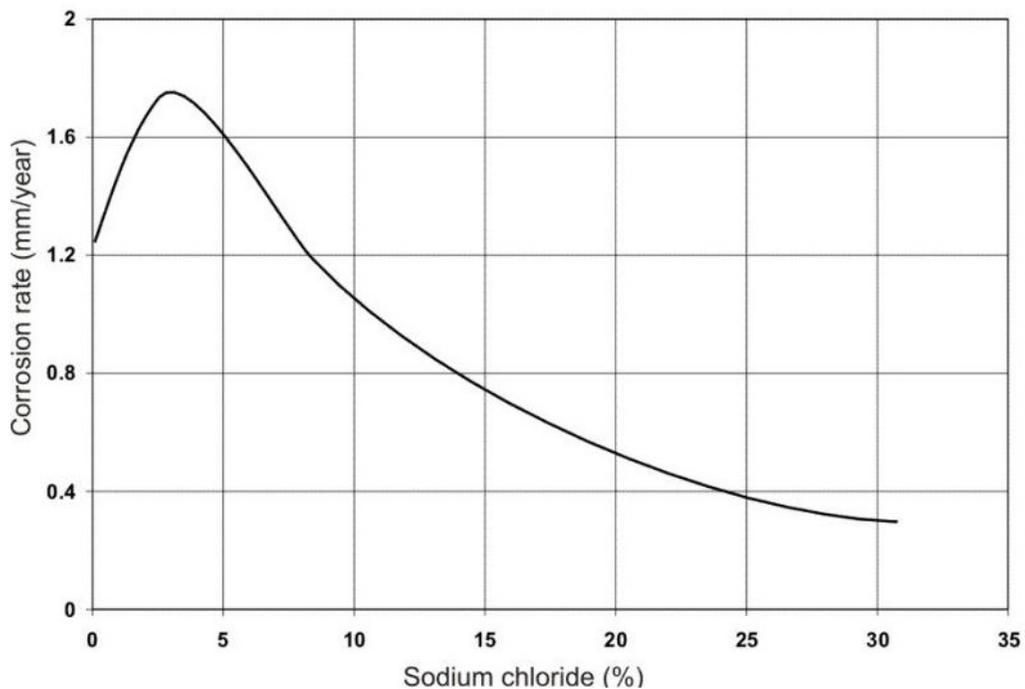


Figure 56: Corrosion rate in function of salinity (Roberge, 2010)

Velocity

The velocity of the electrolyte (e.g. the seawater) influences the thickness of the diffusion layer and, hence, the corrosion rate, as illustrated below.

Alloy	Deepest pit	Average corrosion rate		
	(mm)	(mm y ⁻¹)		
	Still seawater	Still seawater	8.2 m s ⁻¹	35-42 m s ⁻¹
Carbon steel	2.0	0.075	-	4.5
Grey cast iron (graphitised)	4.9	0.55	4.4	13.2
Admiralty Gunmetal	0.25	0.027	0.9	1.07
85/5/5/5 Cu Zn Pb Zn	0.32	0.017	1.8	1.32
Ni Resist Cast Iron Type 1B	Nil	0.02	0.2	0.97
Ni Al Bronze	1.12	0.055	0.22	0.97
70/30 Cu Ni + Fe	0.25	<0.02	0.12	1.47
Type 316 Stainless Steel	1.8	0.02	<0.02	<0.01
6% Mo Stainless Steel	nil	0.01	<0.02	<0.01
Ni-Cu Alloy 40	1.3	0.02	<0.01	0.01

Table 6: Effect of the velocity on the corrosion of metals in seawater (Roberge, 2010)

Table 6 provides data on the effect of water velocity on some of the materials commonly used in seawater systems. The second column gives the pitting depth in seawater with 0 m/s velocity while the 3 following columns show the corrosion rate in mm per year when the water velocity is respectively 0 m/s, 8.2 m/s and 35 to 42 m/s. In considering velocity, it is important to note that local velocities may vary considerably from design velocities. This particularly important where features of the system such as small-radius bends, orifices, partly throttled valves or misaligned flanges can generate turbulence and accelerate corrosion (Roberge, 2010).

2.7 Different manifestations of corrosion

The complete list of different corrosion types is very long. Only the corrosion types relevant to corrosion in ballast tanks will be discussed.

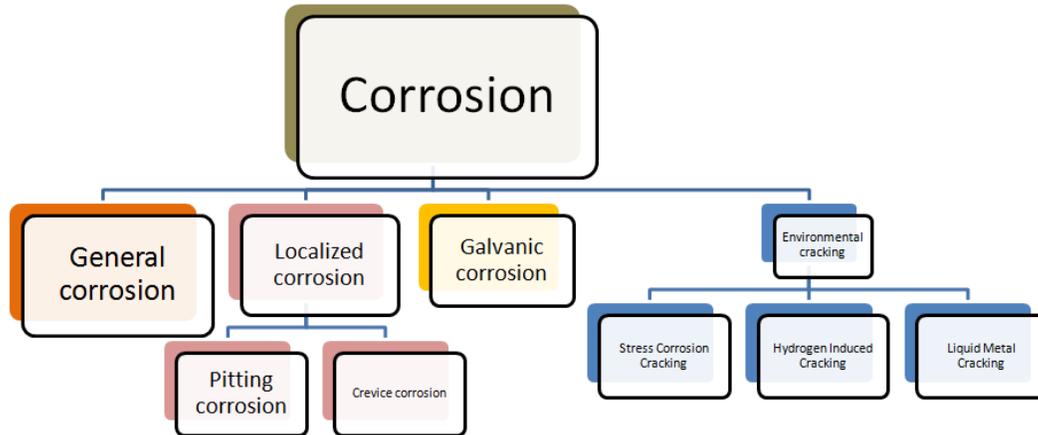


Figure 57: Subdivision different corrosion types (Own work)

The subdivision is based on NACE basic corrosion classes (Dillion, 1982); as represented in figure 57.

2.7.1 General corrosion

Uniform corrosion is characterized by corrosive attack proceeding evenly over the entire surface area or a large fraction of the total area. General thinning takes place until failure. On the basis of tonnage wasted, this is the most important form of corrosion (Roberge, 2000).

3 categories are distinguished (Dillion, 1982) (see also figure 35).

Category I

The electrode potential of the metal in its environment and the kinetics of the reaction between the metal and the environment, determine the corrosion rate of the metal. For example, black steel in oxygen-rich salt water

Category II

A passive barrier coating develops on the surface of the metal, which affects the rate of corrosion of the metal. Corrosion of the metal does not stop completely, but it is usually decreased considerably. The protection offered by the passive barrier coating is different for different environments.

Category III



Figure 58: General corrosion in the ballast tanks of the Algoma Guardian, 25/09/2009

The corrosion rate of the metal in an environment is small enough for the metal to be considered "immune" to attack in that environment.

2.7.2 Pitting corrosion

Pitting corrosion takes the form of deep and narrow corrosive attack, which often causes rapid reduction of the wall thickness.

Pitting corrosion is considered much more dangerous than uniform corrosion since its rate is 10-100 times higher.

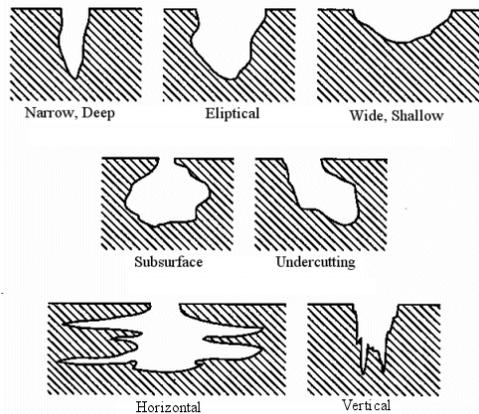


Figure 59: standard visual chart for rating of pitting corrosion according ASTM-G46

Alloys most susceptible to pitting corrosion are usually the ones where corrosion resistance is caused by a passivation layer: stainless steels, nickel alloys, aluminium alloys. Metals that are susceptible to uniform corrosion in turn do not tend to suffer from pitting. Thus, regular carbon steel will corrode uniformly in sea water, while stainless steel will pit. Addition of about 2% of molybdenum increases pitting resistance of stainless steels.

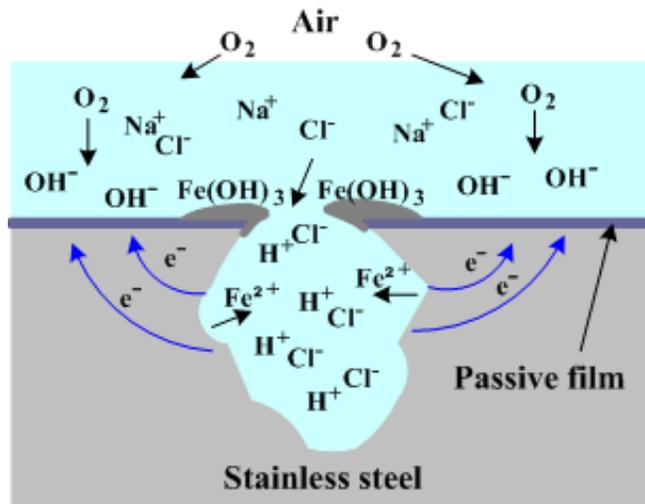


Figure 60: Pitting corrosion (Kopeliovich, 2009)

2.7.3 Galvanic corrosion

Galvanic corrosion occurs when two metals with different electrochemical potentials or with different tendencies to corrode are in metal-to-metal contact in a corrosive electrolyte (Ahmad, 2006).

Galvanic corrosion is affected by the difference in electrical potential between the dissimilar metals (or non-metal as in the case of carbon or mill scale), ratio of the surface areas, the conductivity of the electrolyte, the corrosion product films, the effect of the distance between anode and cathode and the geometric factors being the insulation distance between anode and cathode and the manner of interaction caused by two independent interacting galvanic couples (Jia, 2005).

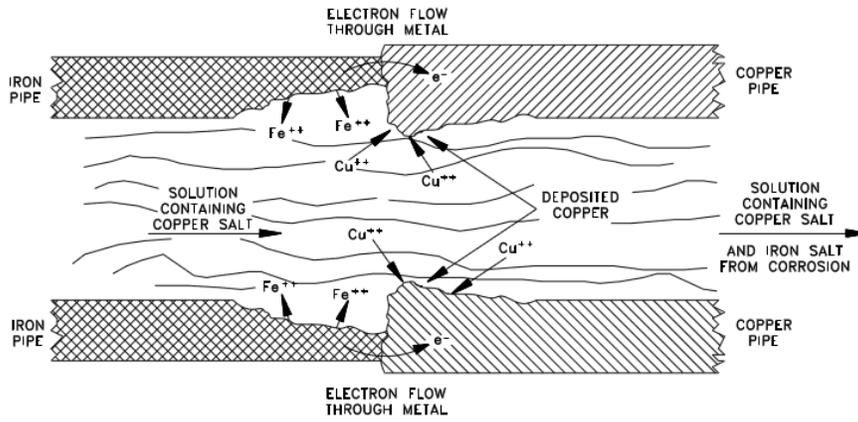


Figure 61: Formation of galvanic cell by joining of two dissimilar metals (U.S. Department of Energy, 1993)

3. Steel qualities used in ship-construction

3 Steel qualities used in ship-construction

3.1 Introduction

Steel is the most important engineering material because it is cheap, easy to produce and relatively strong (Federal Highway Administration, 2002).

The steel used in ship construction is carbon steel and consists out of an alloy of iron (Fe) and carbon(C).

The concentration of carbon determines the physical properties of the alloy. Below 2% ³³ carbon by weight (w/w) the alloy is called carbon steel. If the concentration carbon exceeds 2.5% by weight we call the alloy cast iron.

Carbon Steel	Carbon % (w/w)	Application and properties
Low carbon steel	<0.1%	Soft, ductile. Easy to shape.
Mild steel	0.1 – 0.25%	Low tensile strength, but it is cheap and malleable; surface hardness can be increased through carburizing.
Medium carbon steel	0.25 – 0.45%	Balances ductility and strength and has good wear resistance; used for large parts, forging and automotive components
High carbon steel	0.45 – 1.0%	Very strong, used for springs and high-strength wires.
Ultra-high carbon steel	1.0 – 1.5%	Very hard – used for knives and punches. Usually anything over 1.2% would be made with powder metallurgy and is considered a high alloy carbon steels.
Cast iron	2.5 – 4.0%	Lower melting point, easy casting, lower toughness and strength than steel.

Table 7: Carbon concentration in different carbon steels (NSW Tafe Commission, 2008)

³³ In practice below 1.5% for reasons of forgeability

Besides carbon, other chemical elements such as manganese, silicon, vanadium, tungsten, molybdenum, chromium or nickel are added to the alloy to change the steel properties.

Iron is an allotropic material. In its solid form it can have several crystal structures for a same chemical composition. Each structure is stable in a well defined temperature range. For example delta-iron with BCC structure in the range of 1,538-1,394°C changes to gamma-iron with FCC in the range of 912-1,394°C. This quality of iron is exploited during the hardening process.

3.2 Crystal structures

In the context of this document two crystal structures are important.

Firstly, there is the Face Centred Cubic (FCC) structure. The FCC has atoms located at each of the corners and the centres of all the cubic faces (left image below). Each of the corner atoms is the corner of another cube so the corner atoms are shared among eight unit cells. Additionally, each of its six face centred atoms is shared with an adjacent atom.

This crystal structure exists only above 723°C and is stable between 910°C and 1,400°C. The space between the atoms is quite large and up to 2.1% C by mass can be dissolved.

Secondly, there is the Body Centred Cubic (BCC) structure. The BCC unit cell has atoms at each of the eight corners of a cube (like the cubic unit cell) plus one atom in the centre of the cube (right image below). Each of the corner atoms is the corner of another cube so the corner atoms are shared among eight unit cells.

The space between the atoms is much smaller. The solubility of carbon is very low (< 0.02% by mass). The BCC structure exists above 1,440°C (δ -iron) and below 910°C (α -iron or ferrite).

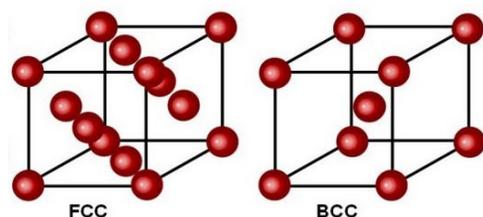


Figure 62: The two unit cell structures typical of metals: body-centred cubic (BCC) and face-centred cubic (FCC) (Dana Ashkenazi, 2007)

The Iron-carbon equilibrium diagram

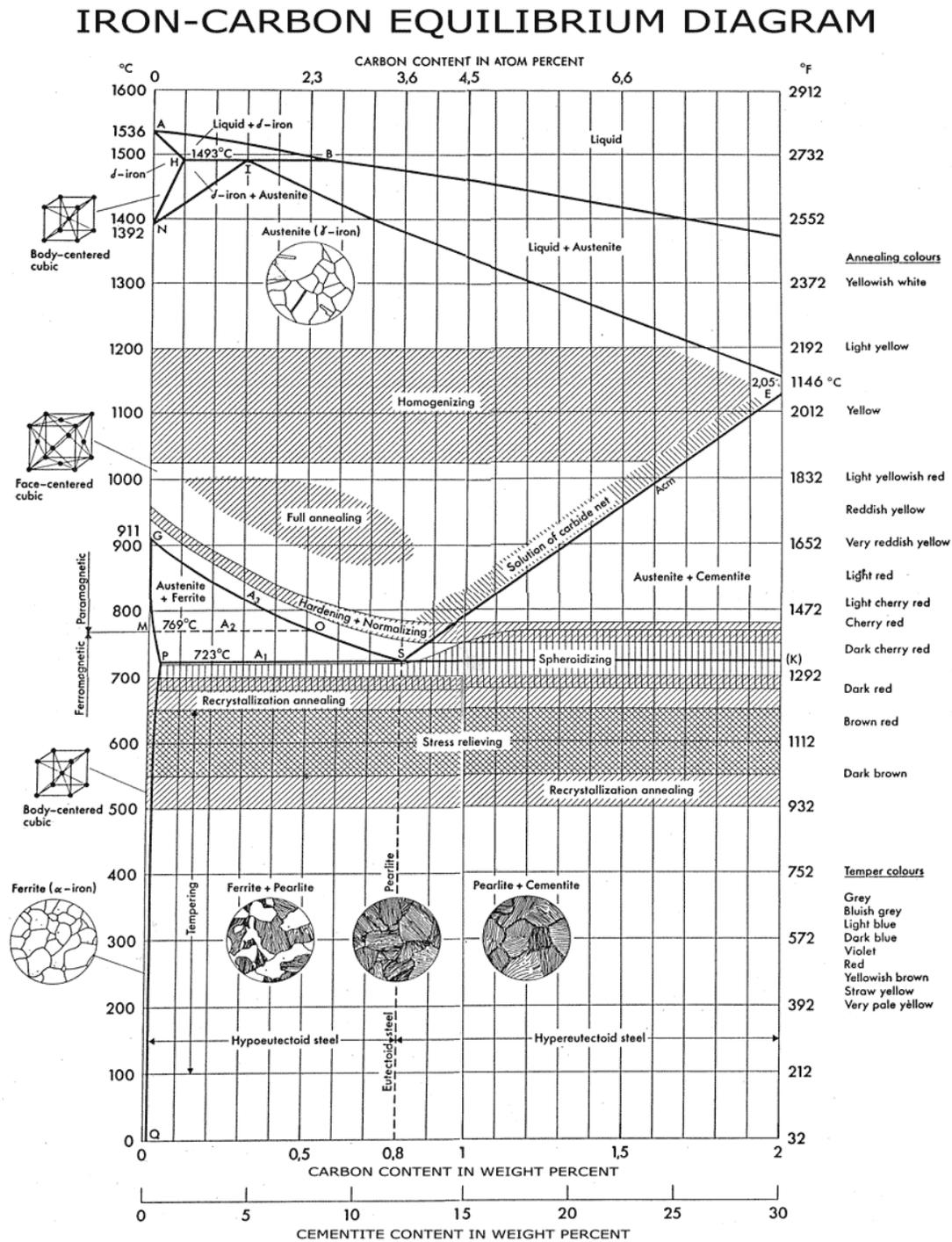


Figure 63: The iron-carbon equilibrium diagram (NSW Tafe Commission, 2008)

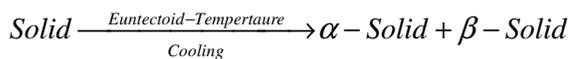
3.3 Eutectoid steel, hypo-eutectoid steel and hyper-eutectoid steel

The iron-carbon equilibrium diagram shows the phases present when Fe-C mixtures are cooled down from a liquid to a solid.

The properties of the steel at ambient temperature are largely determined by the carbon concentration. Distinction is made between hypo- and hyper-eutectoid steel. Situated on the interface between these two we have eutectoid steel that contains exactly 0.83% C and has a 100% pearlite structure.

Figure 63 shows the eutectoid point, generally represented by "S", at the intersection of 723°C and 0.83% carbon.

The eutectoid point is the point where a single-phase solid transforms directly to a two-phase solid.



Austenite => ferrite (88%) + cementite (12%)



pearlite

Austenite- or γ -iron is non magnetic and has a FCC structure resulting in an important solubility of carbon. This feature is of extreme importance in heat treatment, when solution treatment in the γ -region followed by rapid quenching to room temperature allows a supersaturated solid solution of carbon in iron to be formed.

When cooling down from the austenite phase and after annealing the steel will appear in one of the following states: ferrite or α -iron, ferrite + pearlite, pearlite or pearlite + cementite, and this in function of the carbon concentration.

Ferrite contains a very small quantity of carbon. The tensile strength is limited and the hardness is only 80HB³⁴. The toughness is the same as austenite. Ferrite has ferromagnetic properties below 770°C.

³⁴ Hardness according the scale of Brinell. Hardness of mild steel is 120HB; the hardness of aluminum is 15HB.

Cementite is very hard (700HB, 1,200HV³⁵) and very brittle. Material consisting 100% out of cementite is of no use. Cementite is very resistant to abrasion and erosion.

pearlite combines the properties of ferrite and cementite. The hardness is approximately 200HB.

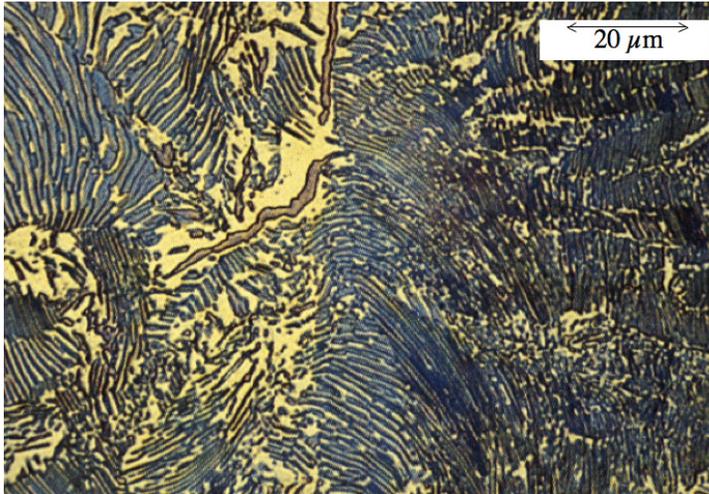


Figure 64: Close-up view of pearlite showing layers of ferrite (yellow) and cementite (dark) (NSW Tafel Commission, 2008)

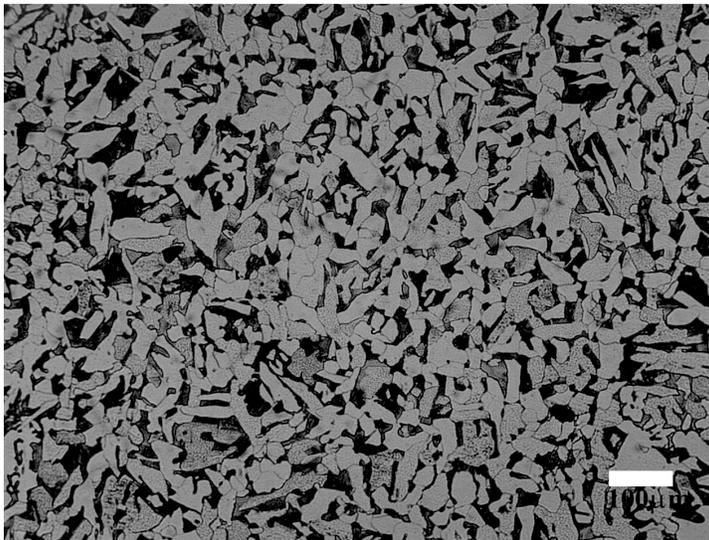


Figure 65: ferrite (light gray) and pearlite (dark gray) in carbon steel A285 (% wt.: 0.18 C, 0.43 Mn, 0.009 P, 0.026 S) (Duncan, 2000)

³⁵ Vickers Hardness

3.4 Classification societies

Classification societies are private organisations. Their objective is to collect data concerning the construction, maintenance and condition of a ship. This information might be of interest to charters, brokers, insurers, maritime inspections, port state control or eventual buyers of a ship. It is collected in a register and published regularly by each classification society.

Classification societies establish and apply technical requirements for the design, construction and survey of marine-related facilities, principally ships and offshore structures. These requirements are published as classification rules – rules and regulations of the classification society.

Classification consists in a representation of the level of compliance of a ship, vessel or offshore structure to the rules set up by the classification society, following surveys carried out by its surveyors as provided for in the rules.

It is represented by a class entered on the classification certificates and transcribed in the register of ships published periodically by this society.

3.5 Steel qualities used in ship-building

Steel for ship's hull construction is usually mild steel containing 0.15 to 0.23 % carbon, and a reasonably high manganese content (0.4-0.7%). Sulphur and phosphorus in the mild steel are kept to a minimum (less than 0.05 % for either component). Higher concentrations of both are detrimental to the welding properties of the steel and cracks can develop during the rolling process if the sulphur content is high (Eyres, 2007).

Ship classification societies originally had varying specifications for steel. In 1959, the major societies agreed to standardize their requirements. There are now five different qualities of steel employed in merchant ship construction and referred to as IACS³⁶ steels. These grades are A, B, C, D and E. Grade A being the ordinary mild steel following Lloyds Register requirements and commonly used in ship building and grade C being to American Bureau of Shipping standards. Grade B is a better quality mild steel than grade A and specified where thicker plates are required in more critical regions. Grade C, D and E possess increasing notch-toughness³⁷ characteristics (Eyres, 2007).

³⁶ IACS: International Association of Classification Societies

³⁷ Notch-toughness: Measure for the expanding-speed of cracks in steel

These A, B, D and E steel grades don't resist corrosion very well but are notwithstanding used for the production of hull plates for ships. They are cheap, easy to produce and relatively strong. (Roberge, 2000)

The mechanical properties of steel can be improved by adding small quantities of other chemical elements. That way high strength low alloy grades have been developed. (Budinski, 2003)

Classification societies denote these high tensile steels are indicated by the by the addition of "H" following the letter indicating the steel quality. Examples are AH, BH, DH, EH

High tensile steel types are stronger than ordinary steel grades but they are certainly more corrosion resistant. Adding minute quantities of chromium, nickel and copper improves this characteristic (Roberge, 2000).

Quality	C	Si	Mn	P	S	Cr	Ni	Mo
A	0.13	0.24	0.66	0.015	0.016	<0.04	<0.02	<0.005
AH	0.18	0.1-0.5	0.90-1.60	0.035	0.035	0.2	0.4	0.08
Quality	Al	V	Nb	Cu	Ti	CE(IIW)	Pcm	
A	0.006	<0.005	<0.005	<0.02	<0.005	0.243	0.172	
AH	0.015	0.05-0.1	0.02-0.05	0.35	0.02	-	0.38	

Table 8: Chemical composition of grade A ship plate steel, 20mm plate (in wt%)³⁸(Okley steel, 2009)

3.6 Micro structure of ship construction steel

Steel grades used in ship construction are generally hot rolled.

The several steel qualities used are classified according a STxx value. (Example ST37 has yield strength of 370MPa)

In general, for ordinary construction purposes (not only ships), cheap steel qualities are used with a carbon concentration between 0.02 and 0.76% (hypo-eutectoid steel). The steel grades are easy to model by rolling.

The micro structure of the ship-building steel is ferrite-pearlite (pers. comm. Prof. J. Lecomte-Beckers, 2/6/2010).

The characteristics of ship construction steel are determined by the production process and the chemical composition.

³⁸ CE(IIW) = Assessment of the weldability, Pcm = Carbon equivalent (Parameter for crack, modified)

Steel making is a two phase project. In a first stage iron ore is melted (reduced) with coke and limestone in a blast-furnace. This molten iron is casted into pig iron that can be stored and transported or the molten iron continues directly to the next step in liquid form.

In the second stage, known as steelmaking, impurities such as sulphur, phosphorus, and excess carbon are removed and alloying elements such as manganese, nickel, chromium and vanadium are added to produce the exact steel required (Mayuram S Balasubramanian & Tarik Afachtal, Masdar, 2010).

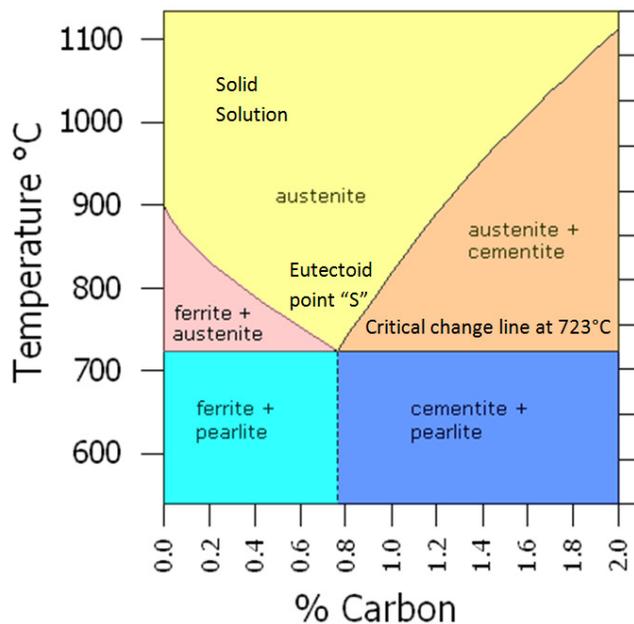


Figure 66: The iron carbon equilibrium diagram (own work)

The figure shows the equilibriums of iron carbon alloys in function of the temperature (vertical axis) and the carbon content (horizontal axis). Ship-construction steel is situated all the way to the left of this diagram seen the low carbon content of 0.15 to 0.23%.

During solidification of a molten metal, different regions are forced to crystallize at the same time. This gives rise to various "grains". Within each grain, the atoms are arranged regularly. It is the spatial orientation of this ordered array that differs between these grains. (Figure 67)

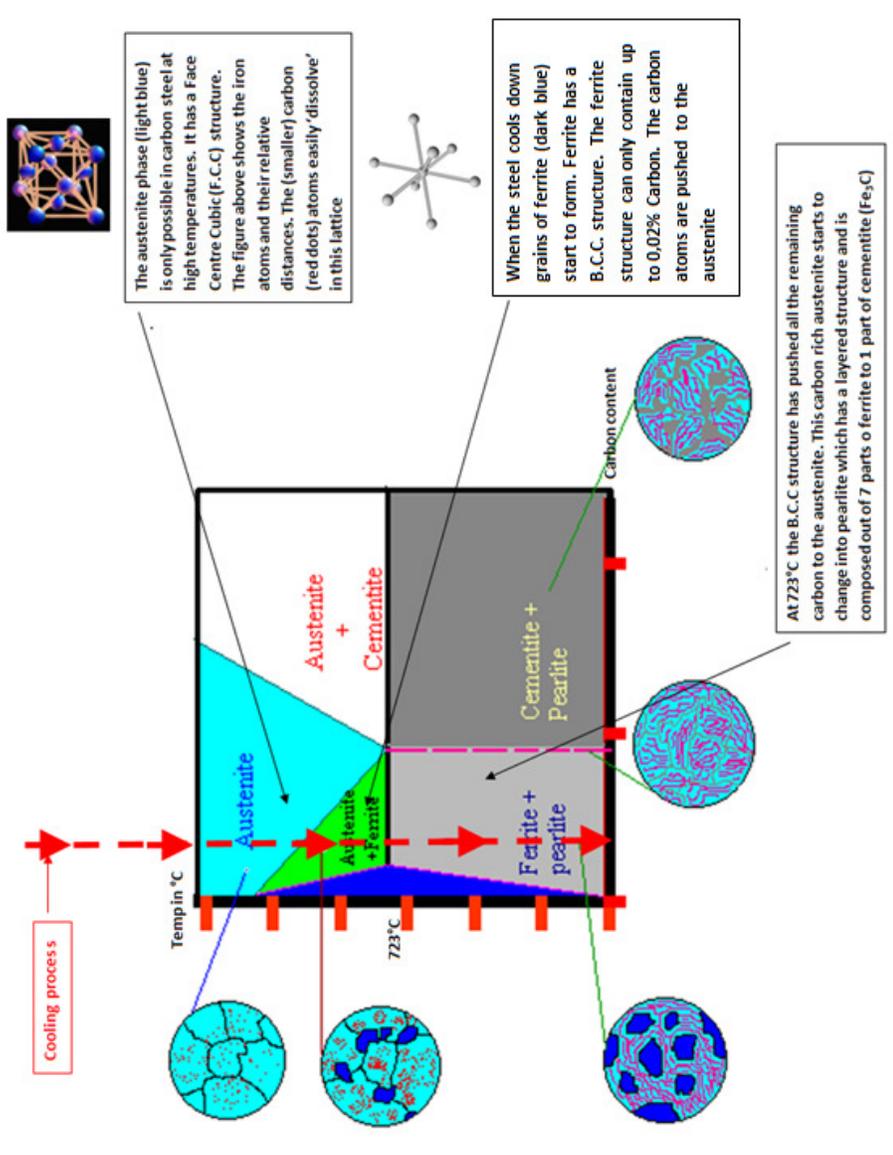


Figure 67: Change in microstructure of the steel while cooling (own work, 2010)

The speed at which this solidification takes place or the chill rate is a very important element determining the final crystal structure of the steel. When cooling down from the melt or high temperature phases, there is an incubation period below the equilibrium melting point or transformation temperature (723°C in the case of the steel shown) before the transformation occurs.

A TTT diagram, T (Time) T (Temperature) T (Transformation) diagram, plots the temperature change in function of the logarithm of time for a given alloy. The diagram shows 2 nose-shaped curves, green and black. The green curve indicates the start of the transformation from austenite to pearlite/bainite while the black curve indicates when the transformation is complete.

Another important element is the temperature M_s , it is the temperature at which the martensite transformation starts.

Martensite is any crystal structure formed by a reaction in which carbon appears to move out of one compound and into another (a single-replacement reaction) (Fewsmith, 2007).

Martensite is the room temperature structure of steel formed as a result of a rapid quench from the austenitic condition. It has a hard, strong, and brittle structure (The Timken Company, 2010).

Martensite is produced at temperatures beneath 220°C

The temperature reduction is coupled with a quenching medium. Water (orange curve) and oil (red curve) produces the fastest temperature drops missing the "nose" of the TTT curve altogether. The temperature decreases so fast that no pearlite and bainite³⁹ are formed.

³⁹ An intermediate transformation product from austenite in the heat treatment of steel. bainite can somewhat resemble pearlite or martensite, depending on the transformation temperature. (<http://www.ndt-ed.org/GeneralResources/Glossary/letter/b.htm>)

Austempering⁴⁰ and martempering⁴¹ are two heat treatments conferring certain mechanical properties to the alloy.

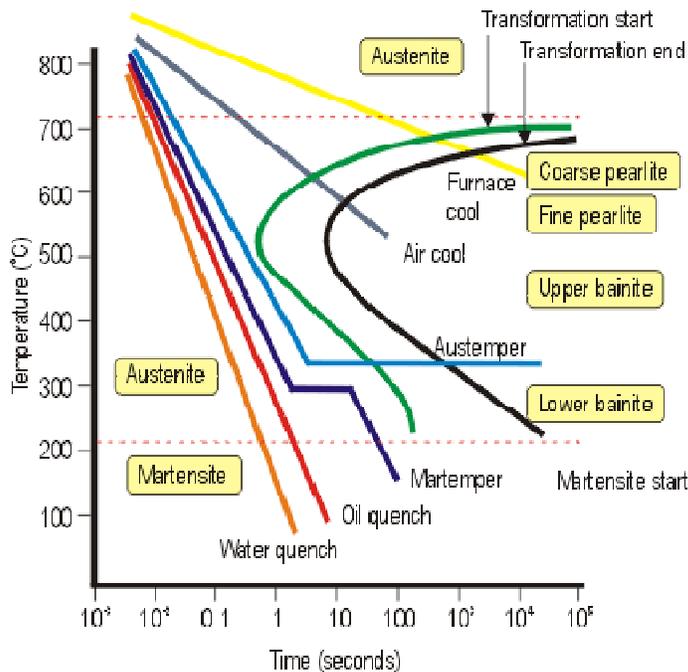


Figure 68: The TTT diagram for AISI 1,080 steel (0.79% C, 0.76% Mn) austenitised at 900°C. (Furness, 2001)

3.7 Influence of the chemical composition of the alloy

The influence of the chemical elements on the mechanical properties of the alloy is given in the next figure.

When not familiar with the mechanical properties of steel it might be useful to consult annex III.

There is no such thing as an alloying element with only positive results. Gaining on one side implicates losing ground on another characteristic.

⁴⁰ Austempering: Quenching from a temperature above the transformation range to a temperature above the upper limit of martensite formation, and holding at this temperature until the austenite is completely transformed to the desired intermediate structure, for the purpose of conferring certain mechanical properties (<http://metals.about.com/library/bldef-Austempering.htm>)

⁴¹ Martempering: A heat treatment involving austenitisation followed by step quenching, at a rate fast enough to avoid the formation of ferrite, pearlite or bainite to a temperature slightly above the Ms point. Soaking must be long enough to avoid the formation of bainite. The advantage of martempering is the reduction of thermal stresses compared to normal quenching. This prevents cracking and minimizes distortion. (<http://metals.about.com/library/bldef-Martempering.htm>)

Alloys are composed to satisfy certain needs. Very often the trial and error method is followed and the outcome is confirmed on an experimental basis.

Apparently it is also very hard to predict the behaviour of an alloy in a certain environment. Once again testing is the only way to get confirmation (personal communication J.P. Smet & De A. Vyt).

Alloying element	Mechanical properties															
	Hardness	Tensile strength	Yield point	Elongation	Reduction of area	Notch Toughness	Elasticity	High temperature stability	Cooling rate	Carbide formation	Wear resistance	Forgeability	Machinability	Scaling	Nitridability	Resistance to corrosion
Silicium	↑	↑	↑↑	↓	=	↓	↑↑↑	↓	↓	↓	↓↓↓	↓	↓	↓	↓	-
Manganese at pearlitic steels	↑	↑	↑	=	=	=	↑	=	↓	=	↓↓	↑	↓	=	=	-
Manganese at austenitic steels	↓↓↓	↑	↓	↑↑↑	=	-	-	-	↓↓	-	-	↓↓↓	↓↓↓	↓↓	-	-
Chromium	↑↑	↑↑	↑↑	↓	↓	↓	↑	↑	↓↓↓	↑↑	↑	↓	-	↓↓↓	↑↑	↑↑↑
Nickel at pearlitic steels	↑	↑	↑	=	=	=	-	↑	↓↓	-	↓↓	↓	↓	↓	-	-
Nickel at austenitic steels	↓↓	↑	↓	↑↑↑	↑↑	↑↑↑	-	↑↑↑	↓↓	-	-	↓↓↓	↓↓↓	↓↓	-	↑↑
Aluminium	-	-	-	-	↓	↓	-	-	-	-	-	↓↓	-	↓↓	↑↑↑	-
Tungsten	↑	↑	↑	↓	↓	=	-	↑↑↑	↓↓	↑↑	↑↑↑	↓↓	↓	↓↓	↑	-
Vanadium	↑	↑	↑	=	=	↓	↑	↑↑	↓↓	↑↑↑↑	↑↑	↑	-	↓	↑	↑
Cobalt	↑	↑	↑	↓	↓	↓	-	↑↑	↑↑	-	↑↑↑	↓	=	↓	-	-
Molybdenum	↑	↑	↑	↓	↓	↑	-	↑↑	↓↓	↑↑↑	↑↑	↓	↓	↑↑	↑↑	-
Copper	↑	↑	↑↑	=	=	=	-	↑	-	-	-	↓↓↓	=	=	-	↑
Sulphur	-	-	-	↓	↓	↓	-	-	-	-	-	↓↓↓	↑↑↑	-	-	↓
Phosphorus	↑	↑	↑	↓	↓	↓↓↓	-	-	-	-	-	↓	↑↑	-	-	-

Figure 69: Influence of the alloying elements on the properties of steel (ODS metals, 2007)

□	Increase
↓	Decrease
=	Constant
-	Unknown

3.8 Rules and regulations of the classification societies and the use of different steel grades.

The “Rules and Regulations of ships” was published by Lloyds Register in 2006. Part 3, Chapter 2, of this publication gives the steel grade to be used for each constructional element of the ship’s hull. It must be pointed out that not all of the classification societies use the same standards and that differences may exist between the societies, as can be seen on the table below.

Lloyds	Norske Veritas	Germanischer Lloyd	Bureau Veritas	American Bureau of Shipping	USSR Register	Nippon Kaigi Kyoka
A	A	A	A	A	A	A
B	B	B	B	B	B	B
D	D	D	D	SS	D	D
E	E	E	E	E	E	E
				CD/DS		
	NV A 27 S					
	NV D 27 S					
	NV D 27 S					
AH 32	NV A 32	A 32	AH32	AH 32	A32	
DH 32	NV 32	D 32	DH 32	DH 32	D 32	
EH 32	NV E 32	E 32	EH 32	EH 32	E 32	
AH 34 S						
DH 34 S						
EH 34 S						
AH 35	NV A 36	A 36	AH 36	AH 36	A 36	
DH 36	NV D 36	D 36	DH 36	DH 36	D 36	
EH 36	NV E 36	E 36	EH 36	EH 36	E 36	
	NVA 40					
	NVD 40					
	NVE 40					
	NVA 420					
	NVD 420					
	NVE 420					

Table 9: Comparison chart of steel standards according to the most important classification societies (Phione limited, 2010)

Further reference material is added in annexes I, II, III.

Annex I: Construction steel according to Lloyds Register of Shipping 2006 – Materials – Part 3, Chapter 2, Section 2. This is an example of how a classification society, in this case Lloyds Register, prescribes the use of the different steel grades on board of LR ships.

Annex II: ASTM A 131/A 131 M-89, Standard specification for structural steel for ships. In ship construction, worldwide, these standards are generally accepted and used as a reference.

Annex III: Principle mechanical characteristics of steel. This annex provides useful background information regarding the mechanical properties of steel referred to in figure 69 and annex I and II.

4. In situ study of ballast tank corrosion on ships—part 1

4 In situ study of ballast tank corrosion on ships—part 1

This chapter has been published as Verstraelen, H., De Baere, K., Schillemans, W., Lemmens, L., Dewil, R., Lenaerts, S., Potters, G. (2009) In situ study of ballast tank corrosion on ships—part 1, *Materials Performance*, October 2009, p. 48-51.

See preliminary remarks page 5.

4.1 Introduction

Double hull ships, made obligatory by the Oil Pollution Act (1990), represent one of the most innovative evolutions in tanker design. They are generally safe, solid, and of high quality. The complex structure of a double hull comes with several challenges, however, making the structure also one of the tanker's more vulnerable elements with a large impact on ship performance and reliability (Rauta, 2004). According to the European Maritime Safety Agency (EMSA) (2005), the principal areas of concern in double hull ballast tanks are the accelerated structural corrosion, the performance of the coating, the quality of the construction standards, and the level of inspection and maintenance (EMSA, 2005). Among these factors, corrosion is considered to be one of the major ones, limiting the life span of ships nowadays to ~25 years (Greenpeace, 2009). This life span is due to the harsh conditions under which ships frequently operate (Gardiner, 2003). Some of these conditions are high temperature (Cridland, 2007), the amount of dissolved oxygen in the ballast water (Tamburri, 2002), high humidity (even in an empty ballast tank) (Cridland, 2007), the presence of high concentrations of salts in seawater and the atmosphere (Paik, 2004 & Al-Fozan, 2008), the temperature of the water the ship frequents (RINA, 2004), and the use of inferior quality steel during the construction of the ship (RINA, 2004). Submerged parts of the ballast tank wall (where less oxygen is readily available) will corrode slower than those parts that are not continuously submerged and often have a water film after the tank has been emptied (Cridland, 2007 & RINA, 2004 & ABS, 2007). The ballast ratio (the percentage of the time the tank is filled) therefore impacts the corrosion rate as well (Gardiner, 2003 & Cridland, 2007). Acidic conditions, under aquatic conditions during submersion and under atmospheric conditions when the tank wall is in contact with sulphur dioxide (SO₂), sulphur trioxide (SO₃), or hydrogen

sulphide (H_2S), will increase the cathodic formation of hydrogen gas and impact the overall corrosion rate (ABS, 2007). Corrosion can be caused by factors other than pure physicochemical processes. Over the last two decades, the maritime industry has become increasingly aware of the possible corrosive actions of different groups of bacteria—for example, sulphate-reducing bacteria (SRB) or iron-related bacteria (IRB) (Odon, 1990 & Little, 2007). Moreover, ballast tanks are complex with an extensive amount of welding and many flexible connections (Al-Fozan, 2008). Their shape makes efficient corrosion control rather difficult. The tanks are not easily accessible, and there is a risk of oxygen deficiency inside the tank as well as a toxic or explosive atmosphere. This makes working inside ballast tanks a rather complex operation. Also, there are many structural features (corners, bulkheads, and small areas) that make the total surface area that needs protection rather large (Singh, 2005). This complex structure leads to substandard coating application, and to the occurrence of many structural forces that cause metal stress and subsequent corrosion. This combination of extreme conditions together with insufficient or improper corrosion control leads to excessive corrosion rates in ballast water tanks, and, when not detected in time, to immense damages with devastating consequences on the ship's construction (Lohmann, 2007). Hence, the corrosion of ballast tanks needs to receive special attention.

4.2 Estimation of ballast tank corrosion

The first thing to do is to estimate the extent of corrosion in a ballast tank. This is difficult to do: the environment is unfriendly, the light is scarce and artificial, and large parts of the ballast tank are difficult to access (OCIMF, 2003). Moreover, in situ determinations have to be executed within a limited time to minimize the effects on normal ship operations. Hence, for practical reasons, assessing an amount of degradation within these confines is best performed by means of estimation and is consequently subjective. To limit this subjectivity, the International Association of Classification Societies (IACS) created an internationally accepted corrosion assessment scale (IACS, 2006). This scale consists of a number of diagrams representing a certain percentage of scattered and localized corrosion ranging from 0.1 to 100%. These diagrams allow a fast and easy visual comparison to the conditions in the tank and facilitate a more objective quantification of the corrosion. This assessment scale is accepted worldwide by all classification societies, marine coating manufacturers, and surveyors. According to the IACS standard, a tank condition can be divided into three categories: good, fair, and poor (Table 10) (OCIMF, 2003 & IACS 2006).

Comparison of the IACS standard scale with the systems adhered to by IMO (2002) and Lloyds Register (2005)^{17, 21-22}			
Rating/Condition^(A)	Good	Fair	Poor
Breakdown of coating or area rusted	<3%	3 to 20%	>20%
Area of hard scale	—	<10%	≥10%
Local breakdown of coating or rust on edge or weld lines	<20%	20 to 50%	>50%
Rating/Condition^(B)			
Spot rust and light rust	Minor	>20%	
Edges and welds		Local breakdown	
Hard scale			≥10%
General breakdown			>20%
Rating/Condition^(C)			
Spot rust and light rust	Minor	>20%	
^(A) General IACS Standard Method IACS clarification of “good,” “fair,” and “poor”			
^(B) IMO Res. A.744(18): Assessment of Existing Coating Systems for all Vessels Except Tankers			
^(C) Lloyds Register: Definition of Coating Conditions			

Table 10: Comparison of the IACS standard scale with the systems adhered to by IMO (2002) and Lloyds Register (2005) (IACS, 2006 & IMO, 1993 & Lloyds Register, 2005)

This division offers a practical method to decide whether the ballast tanks are being kept within acceptable safety margins. The tanks have to be maintained in a “good” condition for the ship to avoid an expensive annual re-examination. Such a methodology has the general advantage of offering a globally uniform system. Nevertheless, although a three-level system suffices for inspection and maintenance studies, a research project needs a greater depth of understanding and detail. Therefore, we have established a refinement of the IACS system, presenting a new corrosion index (CI) based upon 10 different corrosion subcategories. In this article and in Part 2 next month, we will show how the CI is able to demonstrate similar patterns as the physical methods of Paik, et al. (2004) (Paik, 2004), proving its worth in establishing in situ the condition of a given set of ballast tanks. Based upon this CI, we will present a methodology to describe the condition of ballast tanks.

4.3 Data collection

4.3.1 Sampling of the ships

The ballast tanks of 65 ships were visited and mud or slime samples were taken for subsequent laboratory analysis. Twenty ships were sampled while in drydock, 37 in port, and eight at sea. Since ballast tanks are considered confined spaces (IMO, 1997), special safety precautions are required before entering. Sufficient ventilation must be available and the air must be fit for breathing. Before each entry, the atmosphere was tested for oxygen and toxic and flammable gases. The confined space procedure was followed to the letter.

4.3.2 Collection of information on ship variables

For this study, a sample data sheet was produced to record all relevant information in a structured way. The data sheet is divided into two major parts: a general section and a tank-related section. The general section contains all ship information relevant to the study:

- The ship's name and age
- The trading area (to obtain the average salinity and the minimum and maximum temperature of the water in which the ship has been sailing)
- The shipping company and the class society
- The country of construction (we defined five different areas: Korea, Japan, China, Europe, and the rest of the world)
- The last item included is the cargo transported.

Some cargoes are heated for transportation. This increase in temperature might affect the general corrosion rate in the adjacent ballast tank, as corrosion increases with higher temperature (ABS, 2007 & AMTEC 2003). The first item listed in the tank-related section is the presence of galvanic anodes. The material and condition of the anode are noted and also an indication of its corrosion protection effectiveness. The condition of the anode is a function of the time since its installation, the corrosion condition of the tank, and the immersion frequency of the tank (ASTM, 2008). The ballast tank coating and date of application are noted.

Information also relevant to the study is the ballasting frequency. A tank that is always dry or completely immersed will have a lower corrosion rate than a tank that is often filled and emptied. Gardiner and Melchers (2003) define ballast ratio as an influencing parameter to corrosion (Gardiner, 2003), together with the trade route and the corrosion control system used. We selected three categories for this study: always dry, wet/dry, or immersed most of the time.

4.3.3 Collection of information on tank corrosion

Ship ballast tanks can be divided into four types: forepeak, after peak, double hull, and double bottom tanks. For each type, a schematic plan is included in the data sheet. Detailed information concerning the concentration of corrosion observed during tank entry was noted on the corresponding form.

Every tank was divided into a maximum of three levels: top, middle, and bottom. When more than three levels were present, the top and bottom level were considered separately while the intermediate levels were combined and regarded as one middle level. The inspection was carried out from top to bottom. At each level, photos were taken of the forward, aft, top, bottom, starboard, and port sides of the tanks. Detailed photos were taken when the inspectors noted a special type of corrosion or an abnormality.

4.4 Conclusions

The work described in Part 1 shows the complexity of developing a corrosion assessment of a ship ballast tank. Ballast tank integrity is essential to the operation and safety of merchant ships. Part 2 (November 2009 MP) will cover the data collection and analysis and the development of a CI for assessment of ballast tanks.

4.5 Acknowledgments

This work has been funded by the BOF research fund of the Antwerp University Association. The authors wish to thank specifically the captain, crew, and management of all visited ships, the staff of Antwerp Ship Repair, and the students that brought in samples during their training period on board. Particular gratitude goes to Evelien Dils and Ludwig Mertens, who aided in the analysis of the data within the frame of their master thesis.

5. In situ study of ballast tank corrosion on ships—part 2

5 In situ study of ballast tank corrosion on ships - Part 2

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See preliminary remarks page 5.

5.1 Quantification of the Corrosion

To understand the extent of corrosion in the entire tank, a CI system was established. Every tank was divided into a maximum of three levels. For each level (1 [top], 2 [middle], or 3 [bottom]), the percentage breakdown of the coating was visually inspected and compared with a list of reference images. The reference images and values are based upon international standards.

Four separate values were noted for each level:

1. The percentage of local corrosion on the flat surfaces (%)
2. The percentage of scattered corrosion on the flat surfaces (%)
3. The percentage of corrosion on edges and welds (%)
4. The percentage of the quantity of rust scale (%)

The percentages of scattered and local corrosion of the plates were added up. The percentages of corrosion on the flat surfaces, edges, and welds and the quantity of rust scale were each translated into a CI as follows:

1) The area of hard scale was considered to be included in the breakdown of coating or area rusted.

2) The percentages of “breakdown of coating or area rusted” (CP) and “local breakdown of coating or rust on edge or weld lines” (CE) were weighted using the following distributive keys based on the percentage of edge corrosion:

$$\text{If } CE \leq 20\% \text{ then } CI = (0.85 \times CP) + (0.15 \times CE) \quad (\text{Equation 1})$$

$$\text{If } 20 < CE \leq 40\% \text{ then } CI = (0.725 \times CP) + (0.275 \times CE) \quad (\text{Equation 2})$$

$$\text{If } CE > 40\% \text{ then } CI = (0.60 \times CP) + (0.40 \times CE) \quad (\text{Equation 3})$$

Following ASTM D610-08.3 we chose a 0 to 10 grading scale (Table 11) and followed the good, fair, or poor subdivisions of the International Association of Classification Societies (IACS). The poorest condition rating sets the CI for the entire tank level. CI = 0 corresponds with an absolutely impeccable state and CI = 10 is analogous with an absolutely disastrous state of the tank.

Key to determine the CI for a given tank level, based upon the percentages of the different types of corrosion				
G/F/P ^(A)	1 > 10 (CI)	Local + Scattered Breakdown of Coating or Area Rusted (CP, %)	Local Breakdown of Coating or Rust on Edges or Weld Lines (CE, %)	Weighted Corrosion (%)
G	0	0	0	0
G	1	0.5	5	1.175
G	2	1	10	2.35
G	3	2	15	3.95
G	4	3	20	7.675
F	5	5	25	10.5
F	6	10	30	15.5
F	7	15	40	25
P	8	20	45	30
P	9	25	47.5	34
P	10	≥30	≥50	38

^(A)G—good, F—fair, P—poor

Table 11: key to determine the CI for a given tank based upon the percentages of the different types of corrosion

A separate corrosion assessment was performed in the immediate area of every spot where mud or slime samples were collected. Although these values cannot likely be correlated with the corrosion related condition of the entire tank, a specific relation between the composition of this mud or slime sample and the condition of the surface immediately around the sample location is more likely to exist. Hence, for each sample location, the percentage of local and scattered corrosion on the flat surfaces was noted, as well as the corrosion of edges and welds and the quantity of scale rust.

5.2 Results and discussion

The CI can assess a ballast tank according to international specifications. Several methods have been developed to help provide a quick and efficient assessment of a given ballast tank. To be acceptable for further use and comparable with existing standards, the CI must correlate with the IACS standards⁴, as well as several others (Table 12). Our CI gives an equally straightforward definition of the good, fair, and poor zones as do the standards referenced above.

Comparison of common rust scales (based upon Lloyds Register [2005])⁵

IACS	ISO	European	ASTM D610	Rusted Area (%)	CI
Good	Ri 0	Re 0	10	0	0
Good	Ri 1	Re 1	9	0.05	1
Good	Ri 2	Re 2	7	0.5	1
Good	Ri 3	Re 3	6	1	2 to 4
Fair	Ri 4	Re 5	4	8	5 to 7
Poor	Ri 05	Re 7	1 to 2	40 to 50	8 to 10

Table 12: Comparison of common rust scales (Lloyds, 2005)

In Figure 70, the good, fair, and poor zones are coloured green, orange, and red, respectively. Furthermore, given the fact that the calculation of the CI is straightforward and its observation is based on 0 to 10 instead of the three definitions of the IACS method, it is our opinion that the CI lends itself well to research purposes.

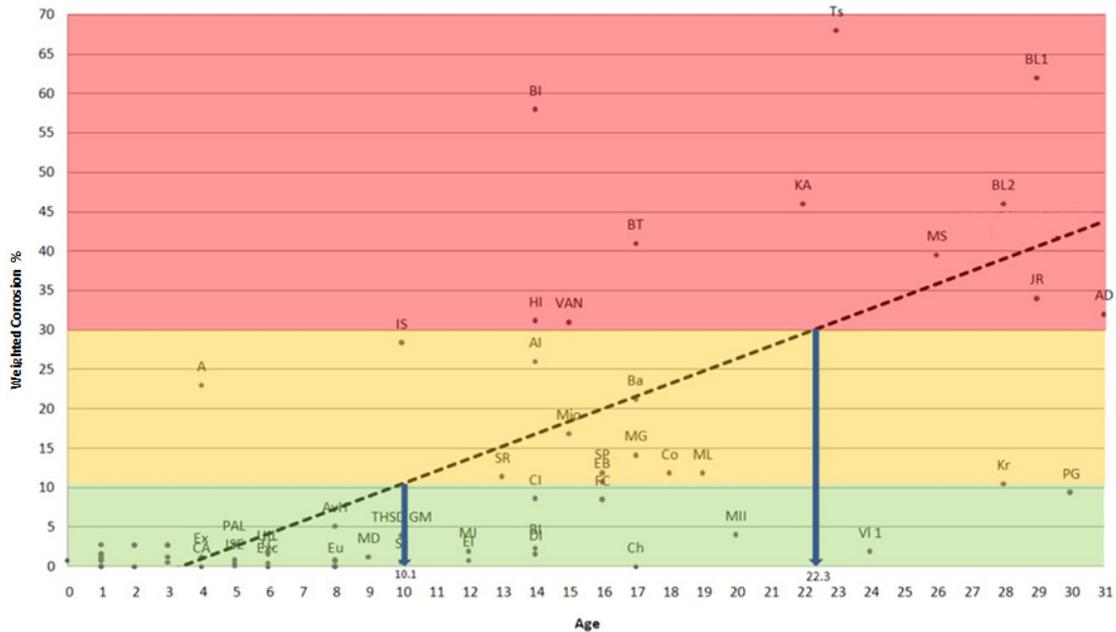


Figure 70: Age-dependency and linear data best describe the corrosion (represented by the calculated CI) of a population of 65 ships. Colours applied in the background correspond with the good, fair, and poor condition as defined by international classification companies. Letter codes represent the different ships present in the analysis. Arrows indicate the estimated average transition from a good condition to a fair condition (at 10.1 years, left arrow) and the estimated average transition

5.2.1 Corrosion is age-dependent

The first analysis that was necessary was the effect of aging on the level of the CI. Figure 70 represents the weighted corrosion % (table 11) as calculated for the 65 tanks that were analyzed, which is expressed as a function of the age of the ship. No significant corrosion was observed in ships younger than 3.5 years. From that moment on, a correlation could be noted between the age of the vessel and the CI. The combination of this linear time-dependency and the classification in good, fair, and poor zones is achieved by determining the intersection of the good-fair-poor zones with the trend line. This demonstrates that the protection systems that are currently in use are able, on average, to maintain a ballast tank in good condition for ~10.1 years. After 22.3 years, the end of coating life is reached (Figure 70).

Our data seem to correlate well with the data from a second database (Soerensen, 2007). This database is based on an inspection of the ballast tank coating condition of 37 vessels. In total, 200 ballast tanks have been inspected. The number of tanks per ship varied from two to 14. Both our data and those from Soerensen and Lang (Soerensen, 2007) can be categorized in four age classes (Table 13), these being the ships that are younger than five years, from five to 10 years old, from 10 to 15 years old, and older than 15 years. Both data show a comparable progression of the corrosion with nearly equal amounts of corrosion and blisters developing on the tank walls. Comparisons in terms of our CI were not possible at the time.

Comparison of existing data (source: O.B. Soerensen, E. Lang,⁴ with permission) with the data obtained in the present study. The numbers in parentheses denote the number of ships with a light-colored coating⁴

Service Period (years)	Soerensen and Lang Database		Our Observations	
	Number of Ships	Corrosion and Blister (%)	Number of Ships	Corrosion and Blister (%)
<5	16 (16)	0 to 0.5	14	0 to 2.7
5 to <10	14 (13)	0 to 4.5	16	0 to 2.8
10 to <15	5 (1)	1.4 to 6.6	12	0.75 to 31.2
>15	0	NA	24	0 to 90

Table 13: Comparison of existing data with the data obtained in the present study. (Soerensen, 2007)

Moreover, our data also correlate with the findings from physical measurements of corrosion depth (Soerensen, 2007 & Paik, 2002).

These authors established that the average degree of corrosion in a given ship can be described as a function of time (as represented in Figure 71):

$$t_r = C_1 \cdot (T_e)^{C_2} = C_1 \cdot (T - T_c - T_t)^{C_2} \quad \text{(Equation 4)}$$

$$r_r = C_1 \cdot C_2 \cdot (T_e)^{C_2-1} = C_1 \cdot C_2 \cdot (T - T_c - T_t)^{C_2-1} \quad \text{(Equation 5)}$$

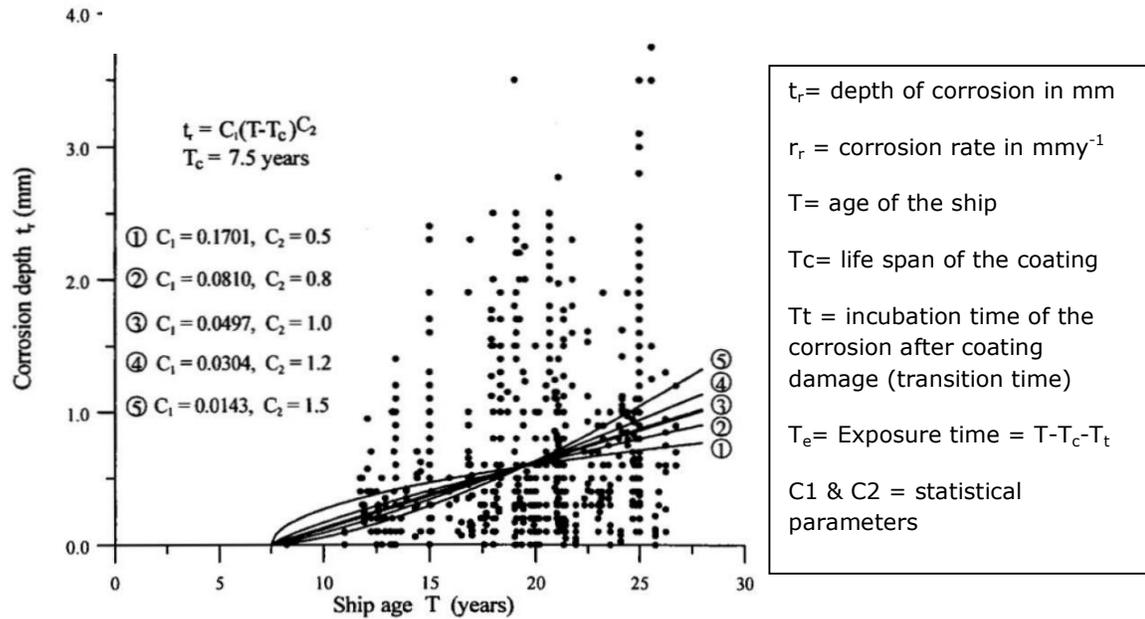


Figure 71: Parameterization of a model for corrosion depth on the outer bottom plating of bulk carrier structures, as a function of ship's age. (Reprinted, with permission, from Paik, et al., 2002) (Paik, 2002)

With t_r being the depth of the corrosion (in mm) and r_r is the rate of corrosion (in mm y^{-1}). T_e represents the time of exposure after the breakdown of the coating (in years), taken as $T_e = T - T_c - T_t$, with T representing the age of the ship (years), T_c representing the life span of the coating (years), and T_t representing the span of a transition period between the actual breakdown of the coating and the first signs of corrosion (years). Finally, C_1 and C_2 are coefficients to be parameterized according to the statistical analysis of the corrosion data.

According to these equations, the degradation progress is divided into three parts—the durability of the coating (T_c), transition (T_t), and the progress of corrosion (t_r). Furthermore, to simplify matters, Paik and Thayamballi assume that corrosion starts as soon as the coating effectiveness is lost and so the transition time is considered zero ($T_t = 0$). C_1 is indicative of the annual corrosion rate while C_2 determines the trend

of corrosion progress. It should be noted that even in the case of Paik, et al., the data showed a too high degree of scattering to allow for a decisive determination of these coefficients. C_1 was assumed at a constant proportion of C_2 , with C_2 typically being situated in the range from 0.3 to 1.0 (and set at $C_2 = 1$). This leaves Equations (6) and (7):

$$t_r = C_1 \cdot (T_e) = C_1 \cdot (T - T_c) \quad (\text{Equation 6})$$

$$r_r = C_1 \quad (\text{Equation 7})$$

These assumptions therefore lead to a linear representation of the strength of aging ships and of the rate of the corrosion progress for an originally coated marine structure.

Comparison of the data by Paik et al. (2004) with the data presented here demonstrates that the temporal distribution of our plate corrosion measurements follows a similar pattern. To start with, Paik et al. (Paik, 2004) use a T_c of 7.5 years. This corresponds very well with the present findings (Figure 70), where the first ships with plate corrosion >10% were at least eight years old.

The right side of the graph could follow Equation (4). For simplicity purposes, C_2 was set at a value of 1 (as was done by Paik et al. as well). In the case of our data, this leads to a value of 1.3646 for C_1 , and hence, for r_r (Equation [7]). An R^2 -value for this correlation was determined at 0.4405. This results in a linear model to synthesize the data on the corrosion after depletion of the durability of the coating, taking into account a transition time of zero. The data presented here are still consistent with this linear model, which, in the authors' view, is the most simple yet entirely practical model, representing the corrosion process with an adequate amount of accuracy.

5.3 Conclusions

By constructing a CI consisting of 10 discrete levels, we have created an instrument for rapid in situ determination of the general condition of a ballast tank. This CI integrates sufficient useful information, and presents us with similar results as comparable research based upon physical methods. We assume that this CI will play a role in further in situ research regarding the corrosion process and the variables that influence this process, either in a positive or negative way. In the data set gathered so far, other significant correlations can be found in addition to age dependency. Enlargement of our current data set, as well as a further exploration on how to demarcate useful age classes within the data, will be necessary.

6. Ballast tank coatings

6 Ballast tank coatings

6.1 Introduction

The application of a coating is the most common anti-corrosion measure for effectively shielding the substrate from the electrolyte (sea water) by an isolating layer.

Each coating system is built up out of different consecutive films.

The first layer is the shop primer. Shop primers are thin coatings which are applied to steel plates and profiles after blast cleaning to provide temporary corrosion protection during transport, storage and production. Sometimes, in function of the paint system chosen, the shop primer is completely removed before painting.

Then an alternating stripe coats and full coats are applied. Stripe coating is a cumbersome process during which edges, welds, scallops, rat holes, man holes etc. are manually painted with brush or/and roller. All places difficult to cover properly by spray application should be stripe coated at least twice to insure adequate coverage and sufficient layer thickness.

The first stripe coat is applied either before or after the first full coat⁴².

The second stripe coat is most typically applied after the second full coat.



Figure 72: Proper stripe coat after the First layer (Dragos, 2004)

⁴² A full coat is covering 100% of the surface and is normally applied by spaying techniques

Beside the stripe coats, one or more complete films of the selected paint are applied. The thickness of these different layers is set by the paint producer. Wet (WFT) and dry film thickness (DFT) are measured continuously by applicator and paint surveyor.

The quality of the paint work depends mainly upon the preparatory work (blasting, cleaning) and the atmospheric conditions at the moment of paint application (temperature and humidity).

A coating system functions both as an active and as a passive corrosion protection. The coating acts as a shield preventing an intense contact between the steel plate and water, oxygen and other chemical substances. Additionally, each ballast tank coating may also contain paint protection components such as zinc phosphate, lead or zinc creating a cathodic protection of the substratum.

6.2 Coal tar epoxy

Until 1990 it was not unusual to leave a ballast tank uncoated. Corrosion in the ballast tanks was not considered to be a major problem. If, in that period, it was decided to coat the tank anyway the traditional coating was dark brown/black coal tar epoxy. This is a two component paint, consisting of epoxy resin and polyamide or amino/polyamide hardener, that provides excellent resistance to crude oil, fuel oil, and sea water.

The application is not particularly demanding. The steel plate must be dry and clean and adequate methods must be employed to remove dirt, dust, oil and all other contaminants that could interfere with adhesion of the coating. Generally two full layers were applied with a DFT of 400 microns each (value only indicative) (Berendsen, 1989).

Coal tar epoxy paints were banned from ballast tanks for two main reasons. Firstly, coal tar resin contains potent carcinogens such as methylcholanthrene, 3,4-benzopyrene and 1,2:5,6-dibenzanthracene (Anstadt, 1989). Secondly, coal tar is black, making a survey in coal tar epoxy coated tanks far from effective. Therefore, the more intensive survey regime called for light coloured tanks, preferably coated by epoxy and preferably a multi-coat system (Soerensen, 2007).

The reputation of this coating type is excellent. In the course of our in situ research we recorded that coal tar epoxy coatings start failing after 3 years, a bit sooner than epoxy or modified epoxy coatings and that the corrosion curve is a shade steeper (See 7.3.2).

On the 8th of December 2006, IMO adopted amendments to the Safety of Life At Sea convention (SOLAS 74/78) by resolution 216(82) of the Maritime Safety Committee. This resolution mandates compliance with the new IMO "Performance Standard for Protective Coatings for dedicated seawater ballast tanks in all types of ships and double-side skin spaces of bulk carriers" (IMO PSPC).

IMO PSPC aims for a 15 year target life. An approved coating should keep the tank in GOOD⁴³ condition for the complete period. No new or uncertified paints may be used.

The ballast tanks coatings must be epoxy and the topcoat must be light coloured.

A thickness of 320 µm is required and the system has to comply with 90/10 rule (no measurement to be below 90% of specified DFT without repair and not more than 10% of measurements to be in the range of 90-100% of the specified DFT without repair). 2 coats and 2 stripe coats must be applied (IMO PSPC; Resolution MSC. 215(82)).

PSPC aims to extend the coating life by paying more attention to primary and secondary surface preparation, edge and weld preparation, curing procedures, inspectors, inspection regimes and record keeping.

6.3 Pure or modified epoxy

Pure or modified epoxy is the compulsory paint system in new built ballast tanks.

"Pure epoxy" is defined as two-component epoxy paint where no additional binder components are added.

"Modified epoxy" is considered as a complement to pure epoxy, i.e. two-component epoxy paint with addition of binder such as coal tar, hydrocarbon resin substitutes for coal tar, vinyl and acrylic binders. As soon as light coloured coatings were requested by ship owners and classification societies during the first half of the 1990's, other hydrocarbon resins began to substitute coal tar – these products were sometimes designated "bleached tar epoxy" (Scheibel, 2003).

Epoxy coatings, in general, are known for their excellent adhesion to steel, very good corrosion protection, good chemical and solvent resistance and for providing hard, abrasion resistant films. Of course, epoxy chemistry is

⁴³ "GOOD" is defined as a condition with spot rusting on less than 3% of the area under consideration without visible failure of the coating. Rusting on edges and welds must be less than 20% of edges or welds in the area under consideration.

so diverse that these properties may vary significantly between different formulations. The experienced formulator can vary many properties, including cure time, chemical resistance, flexibility, pot life and film build according to the requirements of the particular market area (Winter, 2004).

6.4 New developments ballast tank coatings

Epoxy-based paints are the backbone of the marine coating industry. Most probably this will remain so for the next few years, although alternative paint systems are surfacing. The use of polyurethanes seems to offer the best perspectives. A big advantage of these urethane based paints is that curing time is short and predictable allowing a shorter painting cycle during the construction (Safinah, 2009).

Also notable are; the development of solvent free epoxy paints because they are better for the environment and the health of the applicators and the incorporation of luminous elements in the paint allowing a better an easier inspection of the coat integrity.

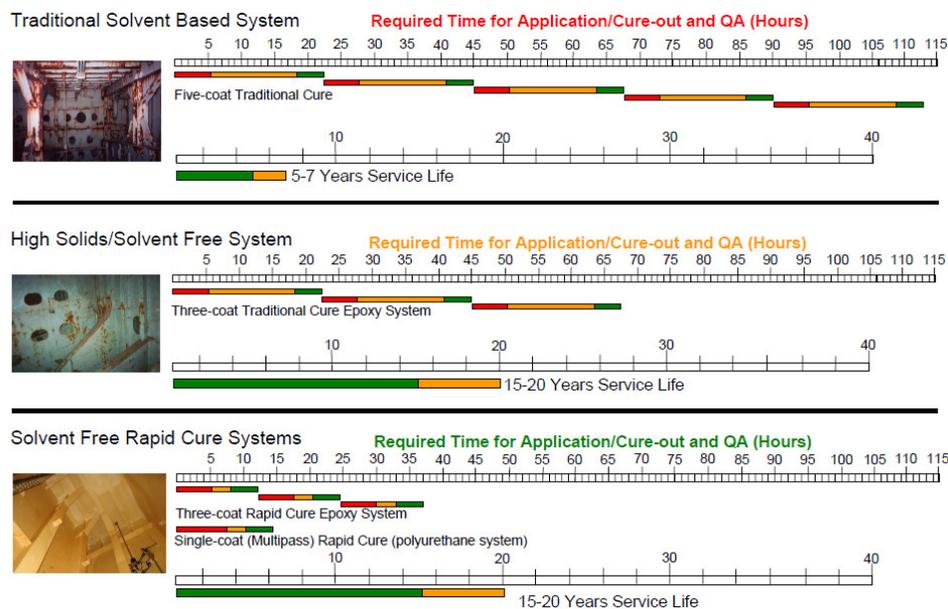


Figure 73: Curing and lifetime of solvent free epoxy and polyurethane paint systems (Office of Naval Research, 2007)

7. Impact of tank and operational parameters on the corrosion in ballast tanks on board of merchant vessels

7 Impact of tank construction parameters on the corrosion in ballast tanks on board of merchant vessels

This chapter has been published as De Baere, K., Verstraelen, H., Lemmens, L., Dewil, R., Lenaerts, S., Potters, G. (2010), Impact of tank construction on corrosion of ship ballast tanks, *Materials Performance* 49, May 2010, p. 48-53.

See preliminary remarks page 5.

7.1 Introduction

From the moment ships were constructed in steel (starting with the SS Great Britain, built in 1843 (Corlett, 1990) around 165 years ago corrosion has been an issue. Until the last quarter of the 20th century, however, this problem was controllable, given proper maintenance was applied to the surfaces of the ship that were most exposed to corrosive conditions. As a consequence of the Oil Pollution Act in 1990 (OPA, 1990 & Ketkar, 2002)⁷ and MARPOL Annex I (IMO, 2006 & Daidola, 1997 & Anonymous, 2006), it became mandatory to construct ships with a double hull. Henceforth, the corrosion problem entered another era. Double hull areas are especially vulnerable to corrosion because they are alternating wet and dry, the coating application is very difficult and a nightmare to keep in good condition (Eliasson, 2005). Moreover, along with this evolution the wet surface of the ballast tanks increased with a factor 2-2.5 (Rauta, 2004) and so did the corrosion trouble. Even more so - the condition of the ballast tanks of a ship serves as a parameter to decide if a ship will continue to sail or will be sent to the scrap yard.

The classification societies use a standard scale to present the condition of the tank and so impose a certain inspection regime. To this end, classification societies use three parameters to describe the tank state: (a) the % corrosion on plates and (b) the edges and (c) the % of scaling corrosion throughout the tank. When the condition of the tank is deteriorating a more stringent inspection system becomes applicable. If the condition of a tank is "GOOD" only surveys during the regular dry docks are compulsory. As soon as the condition turns into "FAIR" a yearly

monitoring is imposed. The condition "POOR" should never exist and could cause retention of the ship (ABS, 2007).

However, the use of multiple parameters makes the statistical interpretation more intricate. A first step facilitating the in situ study of tank corrosion was therefore the development of a novel corrosion index (CI), representing the tank condition with one number only (Verstraelen, 2009) which has enabled us to assess corrosion *in situ* in a number of ballast tanks, on board ships of different origin and age. The basis of this CI, though, is still the internationally accepted IACS standard but with the individual parameters logically weighted.

In this article, we wish to demonstrate a proper statistical methodology of dealing with these in situ data, and test this methodology for the effect of several parameters related to the construction of the ballast tank or the entire ship. Plumbing the depths of the corrosion process in this manner might enable us to find a better cure helping to extend the lifecycle of a ship and return an important economical benefit. After all, it was Iver Iversen (Business develop manager of Wilhelmsen Maritime Services), who once said: "The life of a ship is determined by the life of the ballast tanks" (NEI, 2007).

7.2 Data collection

Between mid 2007 and mid 2009, data were collected on a random set of 100 ships, according to the methodology laid out in chapters 4 and 5. Corrosion was assessed by visual inspection (see 5.1) to become the CI as laid out in table 14.

G/F/P	Corrosion index (CI)	Weighted corrosion in %	Breakdown of coating or area rusted (Local)	Breakdown of coating or area rusted (Scattered)	Local breakdown of coating or rust on edges or weld lines	Area of hard rust scale
Good	0	0%	0%	0%	0%	0%
Good	1	1.175%	0.5%	0.5%	5%	0%
Good	2	2.35%	1%	1%	10%	0%
Good	3	3.95%	2%	2%	15%	0%
Good	4	7.675%	3%	3%	20%	0%
Fair	5	10.5%	5%	5%	25%	1%
Fair	6	15.5%	10%	10%	30%	3%
Fair	7	25%	15%	15%	40%	5%
Poor	8	30%	20%	20%	45%	10%
Poor	9	34%	25%	25%	47.5%	12.5%
Poor	10	38%	≥30%	≥30%	≥50%	≥15%

Table 14: Calculation method of CI. (Verstraelen. 2009)

By using this refined version of the internationally accepted IACS (IACS, 2006) standard, and by documenting the observations in every tank with photographic material, the corrosion in each tank was quantified as objectively as possible: the larger part of the inspections was done by the same team in order to minimize the effect of interpretation errors, and in all other cases, this team reassessed all photographs of the survey afterwards to minimize variation due to the inherent subjectivity of simple visual inspection.

To give a general overview of the corrosion in the tanks that were investigated in this study, the data were analyzed initially using a service life model that is based on two assumptions: an initiation time and a propagation time. A common linear model relation for the propagation time is used, allowing for a rapid and accurate assessment of the kinetics of structural failure of the average ballast tank (Verstraelen, 2009). Usage of the service life model in the time frame we are operating in, also allows for the use of classical inferential statistics, such as a straightforward ANOVA. Statistical analysis was performed with the open source package R (for the logit transformation) and with EXCEL, using the built-in formulae and algorithms for the calculation of the Student t-value and the Shapiro-Wilk test for normality. The weak point of this approach is that the estimation of the initiation time can be discussed. In the analysis the linear relationship was assumed for all observations and the initiation time is determined by the intercept with the time axis (4.5 years).

Of course, as the measured CI is a percentage, with a theoretical range between 0 and 100, classic linear regression methods are not completely satisfying as their predictions are not limited to this allowable range. Also, since severely corroded ships are systematically demolished and so disappear out of the population, there is a bias towards structurally better ships in the higher age ranges, causing also a deviation of a straight line (as the service model generates). Therefore we opted for an approach that is complementary to the service model approach, by transforming the data using a generalized linear model (Faraway, 2006 & Wood, 2006). This transformation was done by way of the logit-function

$$\text{logit}(CI) = \ln\left(\frac{CI}{100 - CI}\right) \text{ (Equation 8)}$$

In order to use this model, the ships with a CI of 0 had to be discarded as outliers.

Another important main assumption in this approach that guarantee the validity of all tests is that the data utilised in the analyses follow a normal distribution, since we work with the residuals (the difference between the observed values and the values that are predicted by the linear model). Therefore, to start the analysis of the data, a check was performed on the normality of the distribution of the CI in the residuals using both graphical (Kernel density estimate) and non-graphical methods (Shapiro-Wilk test).

7.3 Data analysis & interpretation

7.3.1 General corrosion rate of merchant ships

To analyse whether any of the investigated parameters has an impact on the degree of corrosion, we have compared the condition of every ship with the average degree of corrosion after a certain period of time. Following the linear model $CI = 1.6817 \cdot t - 7.1449$, we note that coating breakdown starts after approximately 4.5 years, with an average of 1.7% per year. After 10 years, the ballast tank condition passes from "GOOD" to "FAIR" (Verstraelen, 2009). After 22 years, the tank condition can be categorized as "POOR" (figure 74 A). The logit transformed data have been shown in figure 74 B for comparison.

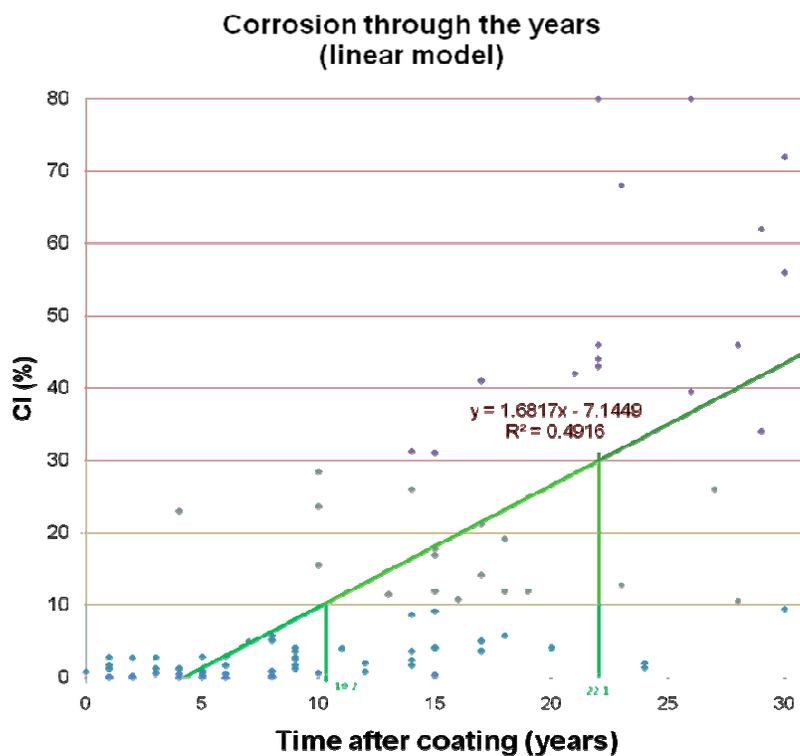


Figure 74 A

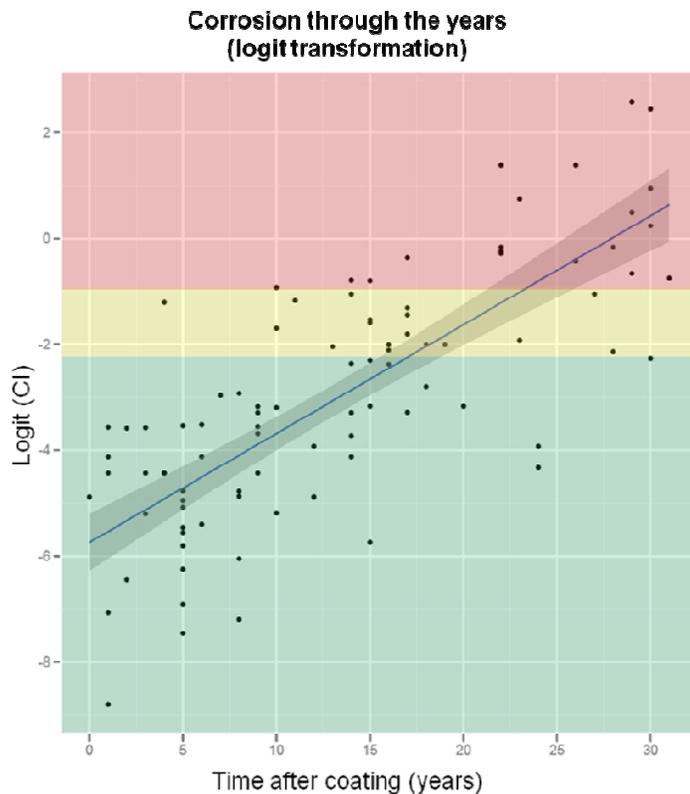


Figure 74 B

Figure 74: General representation of the occurrence of corrosion in function of the time in the ballast tanks of a merchant vessel. A. Regression through the raw data based upon the service life model. B. Generalised linear model after logit transformation of the raw data; the grey zones indicating the 95% confidentiality intervals. The colours in both diagrams indicate the condition of the tank, ships in the green zone being "GOOD", in the yellow zone "FAIR", and in the red zone "POOR", according to the classification by IACS (2006)

As a second approach, we calculated the regression after the logit transformation using the package ggplot2 in R (Hornik, 2009 & Wickham, 2009). The regression shows a 0.005 significance level for both parameters and has an adjusted R^2 of 0.5661.

As to the normality of the data, based on a Shapiro-Wilk test ($P=0.07$), the null hypothesis of a normal distribution could not be rejected (data not shown). This allows for further analysis using more robust parametric statistical tests.

7.3.2 Epoxy - coal tar epoxy

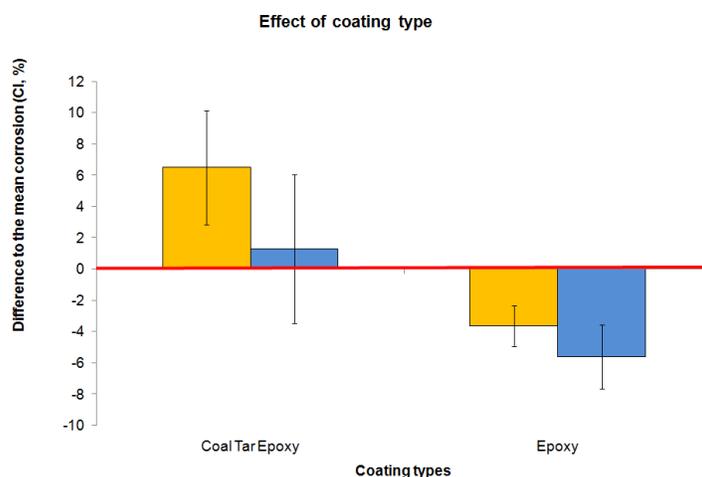
One parameter that may impact the level of corrosion in the ballast tanks is the type of coating that is applied to the tank structure. The introduction of the IMO PSPC SOLAS regulation II-1/3-2 (IMO, 2006 & IMO, 2007) made the use of light colour epoxy coating in ballast tanks

mandatory. Visual inspection of ballast tanks, painted with dark coal tar epoxy was difficult and made an objective quantification of the corrosion almost impossible. Further, the application of the coal tar epoxy held several health risks, such as allergic reactions, asthma-like reactions and cancer (Shimamura, 2002).

During the in situ inspections, 33% of the tanks were found to be coated with coal tar epoxy and 67% with pure or modified epoxy, providing us with two samples that are large enough for further statistical analysis. However, all ships with a coal tar epoxy coating were older than 9 years and there were almost no light coloured epoxy coated tanks older than 22 years. In the range 9-22 years, only 16 vessels had coal tar epoxy coating and 27 had pure or modified epoxy coating. It should be noted that these small numbers restrict somewhat our ability to draw proper conclusions. Hence, following an ANOVA analysis of the residuals (figure 75A) we cannot reject the null hypothesis that the type of coating does not change the time dependent occurrence of corrosion. Analysis of the data using the graphical representation method embedded in the ggplot2 package (figure 75B) supports this conclusion.

As far as the contingent of ships under study here goes, there is no evidence that either coating type is better suited to protect ships. Choosing one type over the other is exclusively a matter of health and environmental considerations. Of course, it will be interesting to see whether any new coatings will prove to be able to lengthen the life expectancy of the merchant fleet worldwide.

A



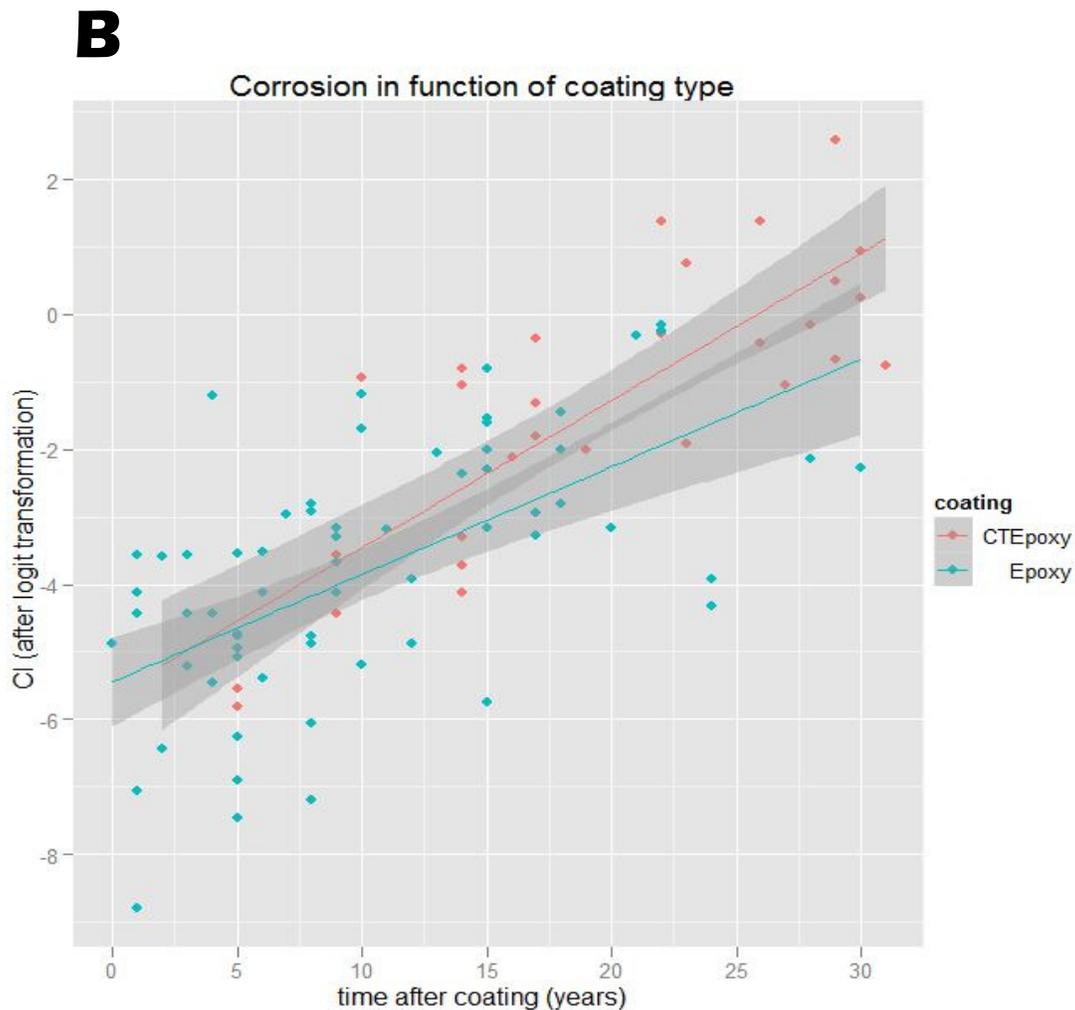


Figure 75: Analysis of the effect of the coating on the occurrence of corrosion

A. ANOVA analysis on the differences between observed corrosion and the amount, predicted by the service life model. Yellow bars: all data, blue bars: data from ships between 9 and 22 years (further explanation see text). Error bars indicate standard error, SD/\sqrt{n} .

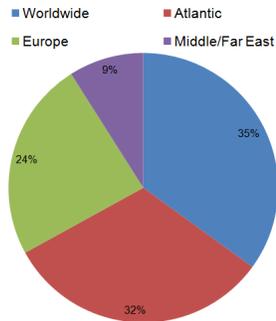
B. Generalised linear model after logit transformation of the data, with the data points categorized per type of coating

7.3.3 Main area of operation

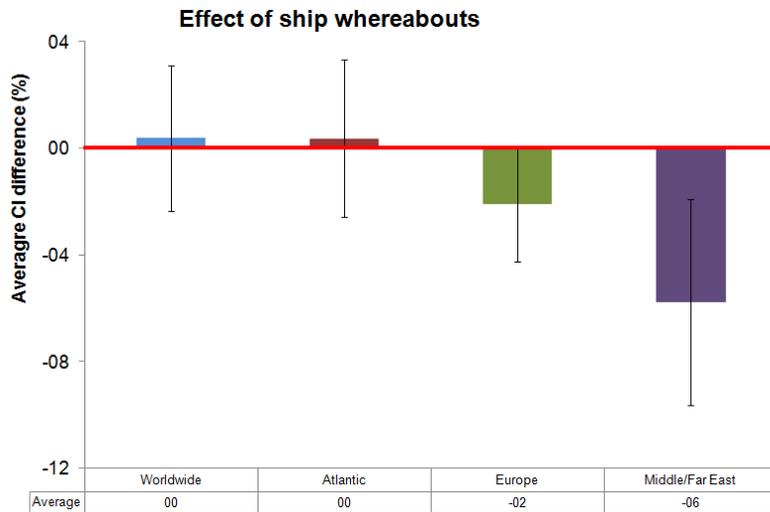
Water temperature is influencing the speed of corrosion; an increase in temperature of 10°C doubles the corrosion speed (Roberge, 2008). It could therefore be expected that the corrosion rate in the tanks will differ with the trading area of the vessels. For this analysis, the ships were divided into four categories: Worldwide trade, Atlantic crossing, Europe and Red Sea-Far East (figure 76A). Again, the average deviation from the service life model was calculated and subjected to an ANOVA (figure 76B). Analysis of these deviations shows that there is no outspoken influence of the area in which the ship is operating on the decay of the ballast tanks

(taken at $P=0.05$ as level of significance). The linear model after logit transformation confirms this outcome (figure 76C). For the Middle/Far East area more data are required to reject the inference that there is no influence of the sailing area.

A



B



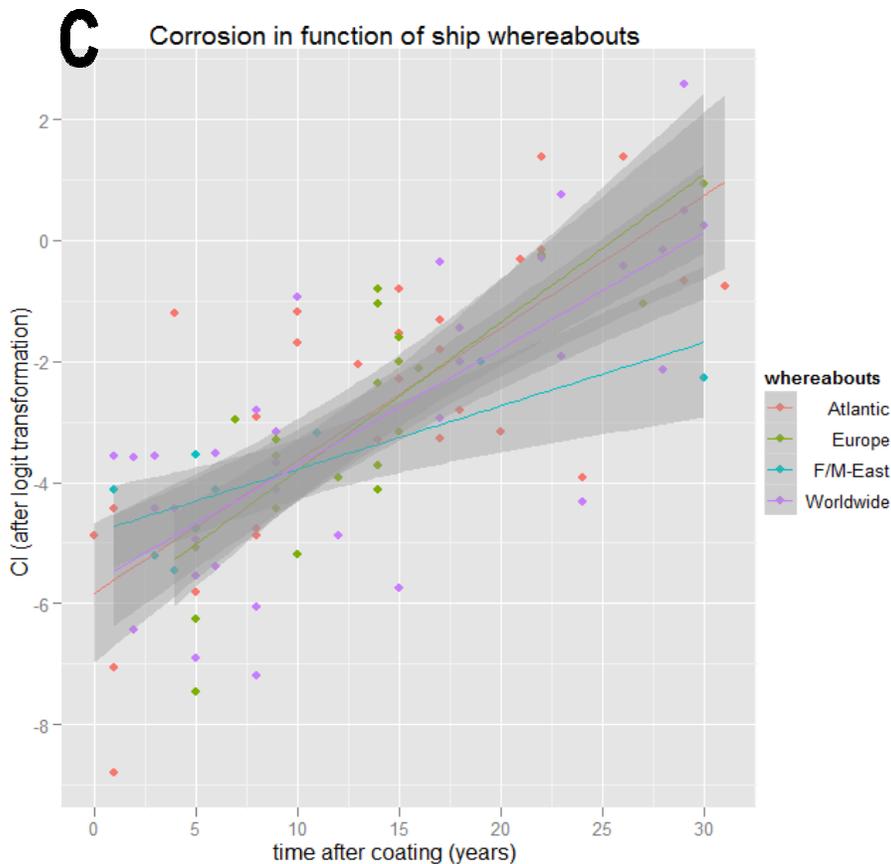


Figure 76: Analysis of the effect of the main trading area on the occurrence of corrosion

A. Distribution of the available data points over the different classes, depicting the main area of operation for the ship

B. ANOVA analysis on the differences between observed corrosion and the amount, predicted by the service life model. Error bars indicate standard error, SD/\sqrt{n} .

C. Generalised linear model after logit transformation of the data, with the data points categorized according to the main trading area of the ship

7.3.4 Ship type

In the database tankers, container carriers, bulk carriers and dredgers are best represented. The other ship types are grouped in a category “other” (figure 77A). One would expect the bulk carriers to be the ships in the worst condition. However, it was not possible to reject the null hypothesis that there is no difference between the different ship types (figure 77B, C). Traditionally, bulk carriers suffer a lot of stress and are treated roughly during loading and unloading operations. The dredgers are performing best but this is largely due to the fact that on board of the ships we surveyed a ballast tank maintenance culture exists. Corrosion was countered with regular touching up of the coating.

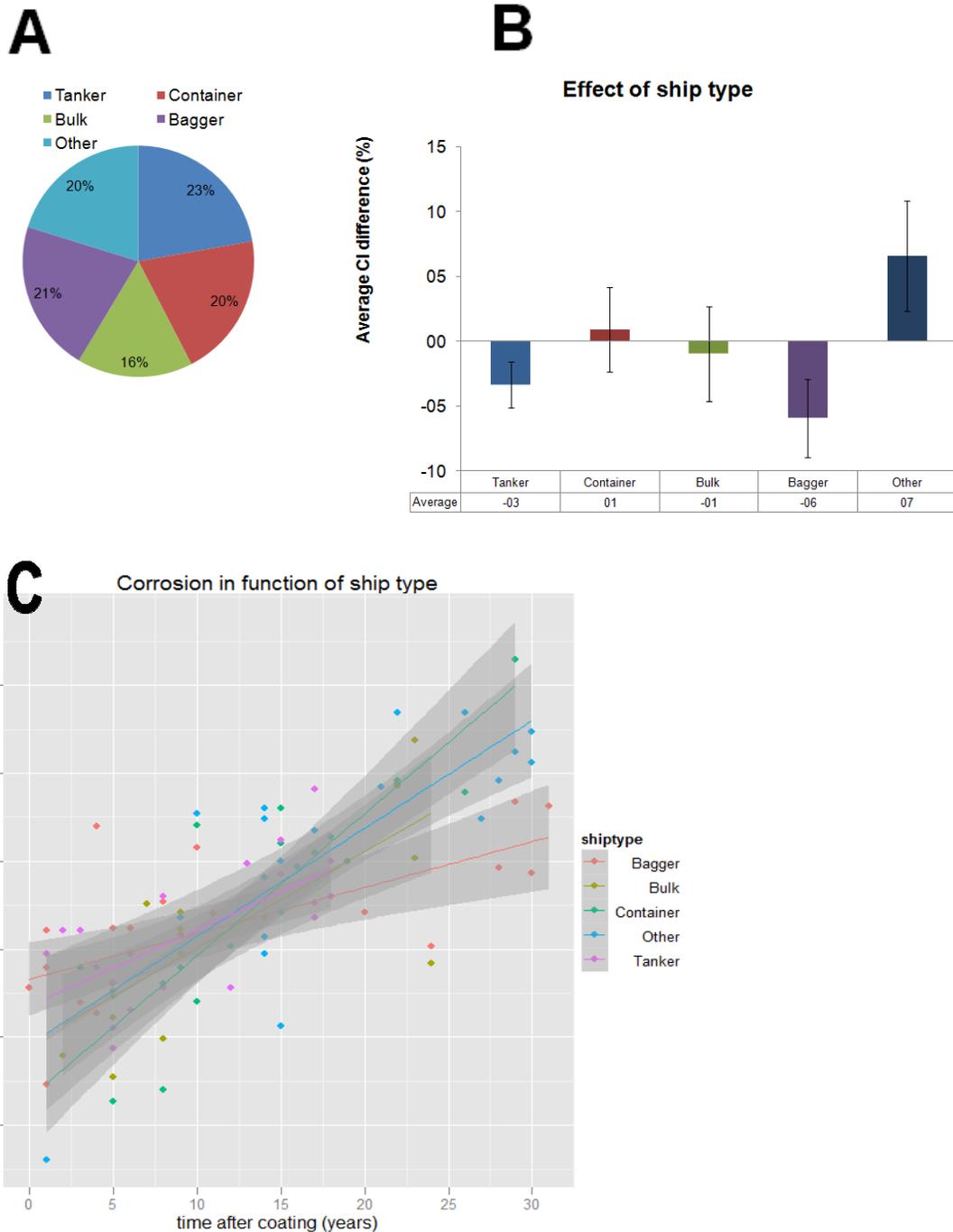


Figure 77: Analysis of the effect of the ship type on the occurrence of corrosion

A. Distribution of the available data points over the different ship types.

B. ANOVA analysis on the differences between observed corrosion and the amount, predicted by the service life model. Error bars indicate standard error, SD/\sqrt{n} .

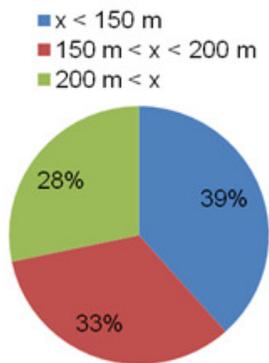
C. Generalised linear model after logit transformation of the data, with the data points categorized according to the type of the ship

7.3.5 Size of the ship

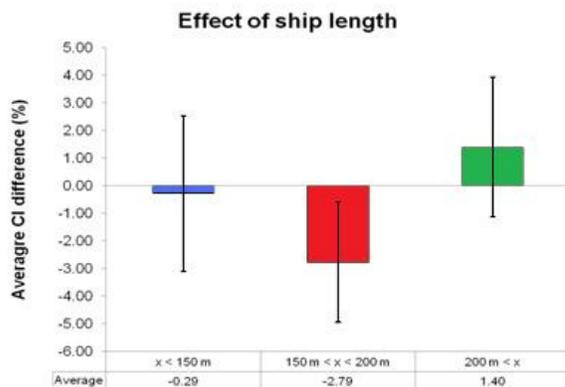
The length is the most representative parameter with respect to the impact of bending forces on the corrosion in the ship's tanks.

Again, the ships in the data set are subdivided in categories. Ships < 150m, which are considered as small ships, ships with a length over all (LOA) between 150 en 200m, being the average sized ships and the ships with a length over all (LOA) > 200m, considered as large ships (Figure 78A). Figure 78B gives the average difference from the mean of the residuals for each length class. ANOVA indicates there is no significant impact of this parameter on the corrosion rate in the tank, and this is backed up by the analysis after logit transformation (figure 78C).

A



B



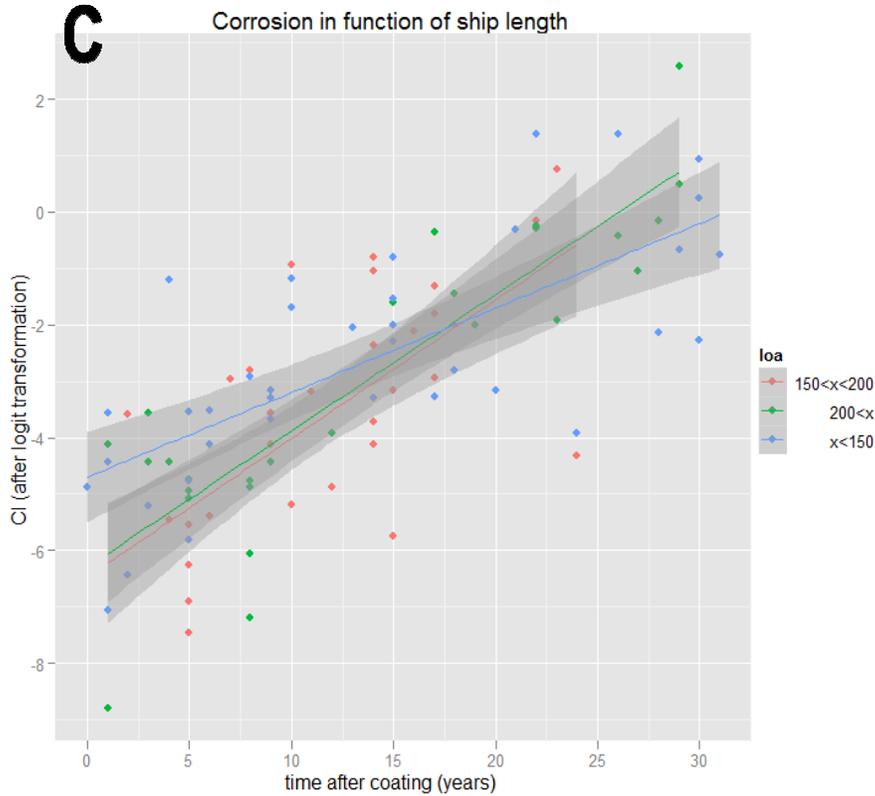


Figure 78: Analysis of the effect of the ship’s LOA on the occurrence of corrosion

A. Distribution of the available data points over the different length classes.

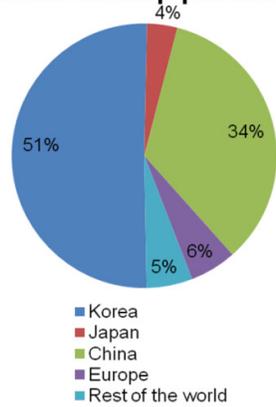
B. ANOVA analysis on the differences between observed corrosion and the amount, predicted by the service life model. Error bars indicate standard error, SD/\sqrt{n} .

C. Generalised linear model after logit transformation of the data, with the data points categorized per length class

7.3.6 Country of construction

The ships are subdivided on the basis of the country of construction. Here our database is not quite representative for the world market: whereas the major shipbuilding countries are well represented in our database, the abundance observed in the database of the different origins differs significantly from the general ships’ population on the world (figure 79). Especially the European vessels are largely overrepresented in our database. Of course, this should not come as a surprise, given the location of the ship repair yard where the majority of the inspections have been done.

A Worldwide ship production



B Ship origins in our data set

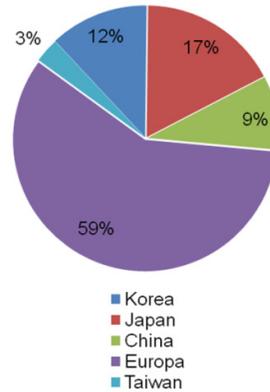
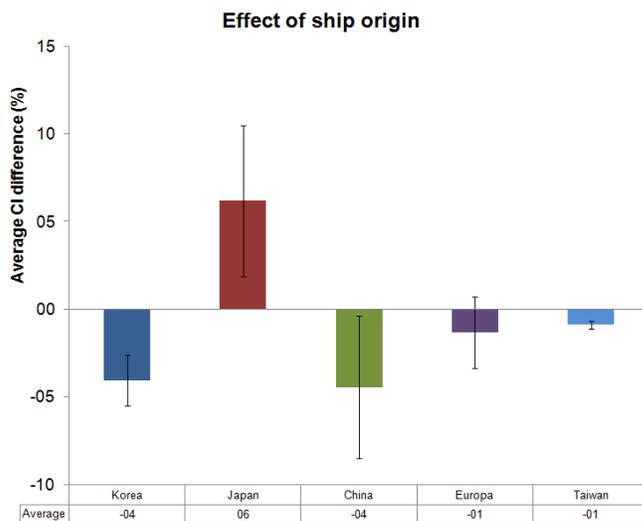


Figure 79: Origin of merchant ships (A) worldwide, and (B) in our data set

The ANOVA test does not indicate any significant differences between the countries of construction (figure 80A). A closer look at the linear model behind figure 80B reveals, that the Japanese ships in our database are apparently significantly more corroded ($P < 0.025$). Removing the small samples (ships from China and Taiwan) from the database only strengthens this inference (now $P < 0.001$; figure 81).

A



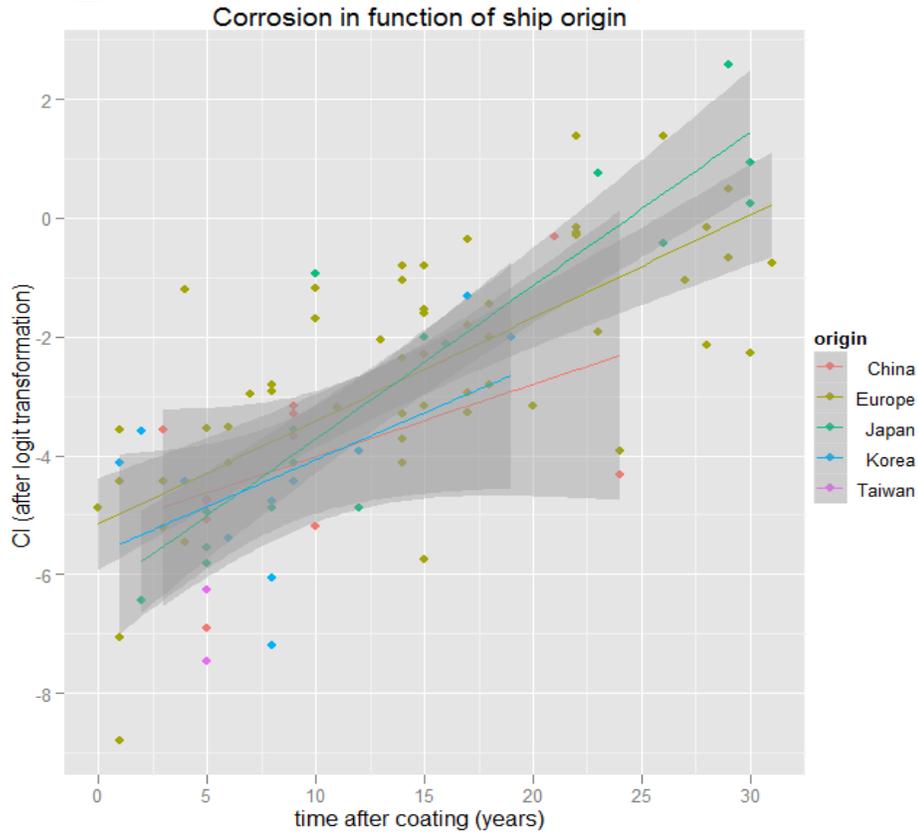
B

Figure 80: Analysis of the effect of the country of construction of the ship on the occurrence of corrosion

A. ANOVA analysis on the differences between observed corrosion and the amount, predicted by the service life model. Error bars indicate standard error, SD/\sqrt{n} .

B. Generalised linear model after logit transformation of the data, with the data points categorized according to the ships' origins

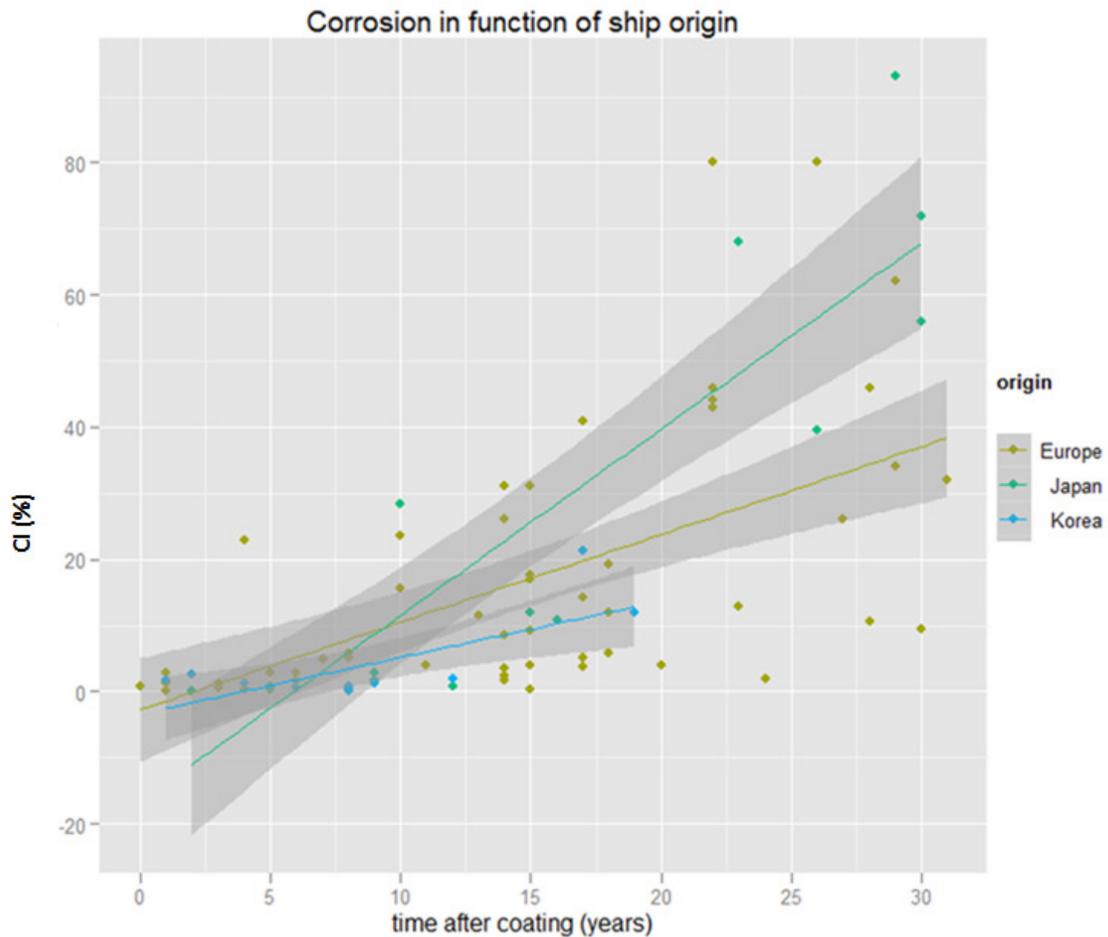


Figure 81: Analysis of the effect of the country of construction of the ship on the occurrence of corrosion, after removal of the smallest populations from the database: generalised linear model of the data, with the data points categorized according to the ships' origins

7.4 Conclusions

The most probable model indicates that most factors have no or a negligible effect on the time evolution of the corrosion index. A classical analysis confirms this for the factors area of operation, ship type and length, and the type of coating. One meaningful difference between ships may lie in the country of construction, and this may well be related to the quality of the steel used. Further research is needed, however, to address these hypotheses.

In any case, we are convinced that the "in situ" aspect of this research is very important and complements well other ongoing, lab based research programs.

8. Protection of ballast tanks using sacrificial anodes.

8 Protection of ballast tanks using sacrificial anodes.

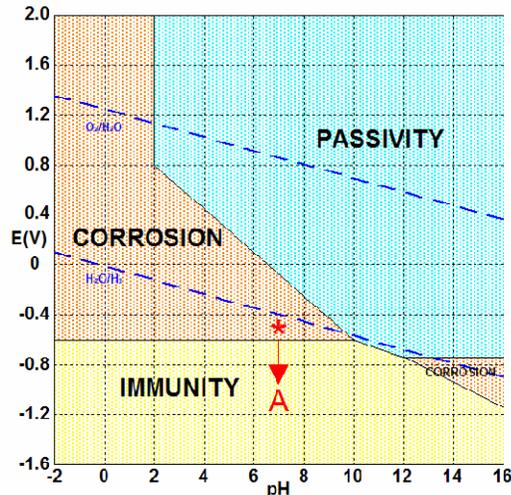


Figure 82: Pourbaix diagram of steel in tap water (Johnsen, 2004)

As exhaustively explained in the chapter “Basic principles of corrosion”, the relation between electrochemical potential $E(V)$, solution pH and the condition of the metal (corrosion, passive, and immune) can be represented in a Pourbaix diagram.

The measured potential for mild steel in sea water (which is a combination of the potential of the anodic and cathodic reactions taking place) is in the order of -640mV (Standard Calomel Electrode).

A pH of 7 puts iron in the corrosive area. The Pourbaix diagram indicates that the corrosion process can be stopped by lowering the potential by shifting the iron into the immunity zone, by approximately 250mV . This can be achieved by connecting the steel plate to a metal with a much lower electrochemical potential (a so-called sacrificial anode) or by applying impressed current as electron source.

The use of impressed current in ballast tanks is forbidden (Amtec, 2008). Too much H_2 could lead to the creation of an explosive atmosphere.

The electrochemical potential of zinc, aluminium and magnesium are all below 1,000mV (SCE) (see figure 83).

When an E(V) of -860mV is reached the corrosion process will stop (ABS, 2007).

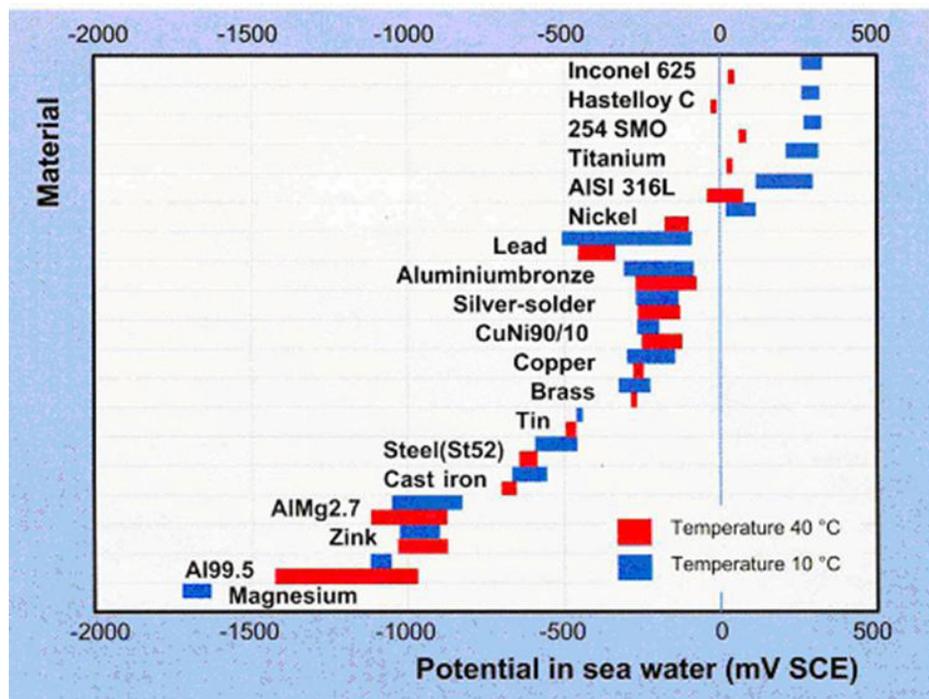


Figure 83: Potential in sea water (mV SCE) (Johnsen, 2004)

When two metals are electrically connected to each other in a electrolyte e.g. seawater, electrons will flow from the more active metal to the other, due to the difference in the electrical potential, the so called "driving force". When the most active metal (anode) supplies current, it will gradually dissolve into ions in the electrolyte, and at the same time produce electrons, which the least active (cathode) will receive through the metallic connection with the anode. The result is that the cathode will be negatively polarized and hence be protected against corrosion (<http://corrosion-doctors.org/CP/Sacrificial.htm>).

Cathodic protection prevents corrosion by converting all of the anodic (active) sites on the metal surface to cathodic (passive) sites by supplying electrical current (or free electrons) from an alternate source (Baxter, 2008).

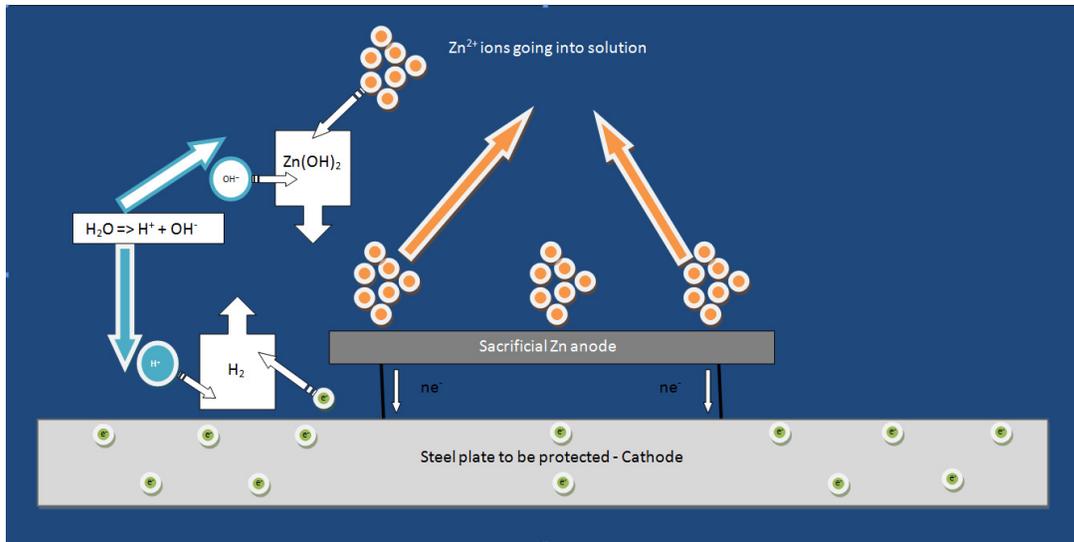


Figure 84: Cathodic protection (own work)



Figure 85: Sacrificial anode in a ballast tanks (own work)

Cathodic protection was first used on board of British warships early 19th century. At that time the wooden hull of the ship was protected with copper sheaths. Iron anodes were used to reduce the corrosion process of the copper plating. Unexpected aspect was that due to the reduced production of copper oxides the fouling and consequently the underwater

resistance increased. (<http://www.corrosion-doctors.org/Corrosion-History/CP-History.htm>)

Anodes, if working well, will be consumed in time. The quantity of anodes in a tank is calculated to last 5 years.

Zinc was the first ever material used to protect steel constructions and is therefore considered as the traditional anode material. However, aluminium has several outstanding values and is picking up lost ground.

To obtain an adequate protection the quantity and the position of the sacrificial anodes in the tank is crucial.

$$I = \frac{A \times i}{1,000}$$

$$wt = \frac{I \times \text{Design life} \times 8,760}{\text{material capacity}}$$

I = Current (A)

A = Protected Area (m²)

i = Current density (mA/m²)

wt = Weight (kg)

Design life: 5 years

Capacity of material in (A.h/kg)

8760 = number of hours per year

The resistivity of the ballast water: 25 ohm-cm is considered in European and Scandinavian waters whilst 15-20 ohm-cm is applicable in Middle and Far Eastern waters (Emirates techno casting, 2009 & NACE, 2007).

Zinc has a capacity of 780 A.h/kg

Aluminium has a capacity of 2,500 A.h/kg

Current densities applicable for various tanks

Cargo/clean ballast tanks	86 mA/m ²
Ballast only and ballast white oil cargo tanks	108 mA/m ²
Upper wing tanks	120 mA/ m ²
Fore and aft peak tanks	108 mA/m ²
Coated surfaces	5 mA/m ²
Lower wing tanks	86 mA/m ²
Double bottom tanks, ballast only	86 mA/m ²
Cargo/ dirty ballast tanks	Dependent on trade

Table 15: Current densities applicable for various tanks (Emirates Techno Casting, 2008)

Some important remarks can be mentioned:

1. Sacrificial anodes only work when they are immersed in an electrolyte for at least 24 hours. Cathodic protection can therefore only be applied to ballast tanks provided that tanks are immersed for 25% of the duration of the voyage (MGDuff, 2009).
2. The areas in the vicinity of the anode will generally receive a higher current density compared with remote locations on the surface. Areas near the anode could also "collect" less current if obstructions are present in the current path between these locations and the anode (http://corrosiontest.its.manchester.ac.uk/lecturenotes/JDS_Notes/throw.htm).
3. Cathodic protection is only effective when the current supplied by the sacrificial anodes is consumed by the steel plate protected. If there is a disproportion the cathode is or not protected sufficiently and will corrode or the steel plate is overprotected and this might damage the coating.
4. Modern coatings are not immune to the effects of cathodic protection. Too many anodes can cause premature coating degradation, paint failure & coatings which delaminate by a process called cathodic disbanding (<http://www.amteccorrosion.co.uk/cathodic.html>).

9. Does sacrifice guarantee a longer life?

9 Does sacrifice guarantee a longer life?

This chapter has been forwarded to Materials Performance for review as De Baere, K., Verstraelen, H., Lemmens, L., Dewil, R., Lenaerts, S., Potters, G. (2009), Does sacrifice guarantee a longer life?

See preliminary remarks page 5.

9.1 Introduction

In general, the use of sacrificial anodes is widespread in all kinds of applications where steel structures risk exposure to a potentially inhospitable environment (Pedefferri, 1996). Also on board of merchant vessels it is common practice to use sacrificial anodes in ballast tanks (Kim, 2007), usually made of zinc (Bird, 1996 & Jelmert, 2000 & Rousseau, 2009), to delay the onset and the further development of corrosion

This use of anodes to counteract the degradation of metal structures is built upon very sound physical foundations (Pedefferri, 1996). In principle, cathodic protection occurs upon connecting the metal to be protected (the steel structure of the ballast tank) to an external anode (made of a less precious metal, i.e. usually zinc), leading to the formation of an electrical DC current so that all areas of the metal surface become cathodic and therefore do not corrode. The galvanic anode will be sacrificed, its material being consumed until, eventually; it must be replaced (figure 86).

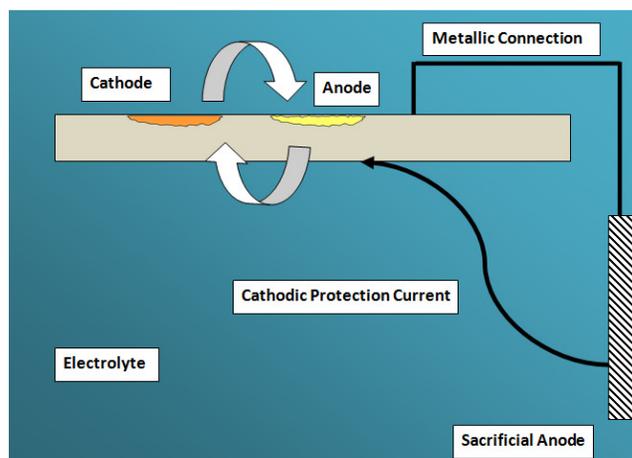


Figure 86: Schematic representation of the working principle of a sacrificial anode (own work)

In more detail, the corrosion will stop if the current intensity (I) is countered with the appropriate counter current (I_{required}). Nominally, a steel surface which is coated with good quality paint will drain in the order of 5mA/m^2 [I_{required}] from a cathodic protection system with an extra 10mA/m^2 to be added for every 10% of the anticipated breakdown over the life of the cathodic system. For example, an exposed steel surface will require 110mA/m^2 [I_{required}] for protection (Botha, 2000); a cathodic protection system that is designed for an anticipated 20% breakdown in tank paint will require a current density of approximately 25mA/m^2 (Botha, 2000). Consequently, the current requirement for a tank will increase with time as the extent of coating breakdown (and thus exposed metal area) increases (AMTEC, 2008).

To determine the required number of anodes to provide the necessary reverse current, the following equation can be used (SSC, 1996).

$$N = (I_{\text{required}})/(I_{\text{anode}}) \quad \text{(Equation 9)}$$

$$I_{\text{required}} = (SA_{\text{total}})(\%PD)(i_{\text{required}}) \quad \text{(Equation 10)}$$

$$\text{Log}(I_{\text{anode}}) = 0.727 \text{Log}(ASA) + \text{Log}(E) - K \quad \text{(Equation 11)}$$

with I_{required} being the required reverse current for cathodic protection based upon the total surface area to be protected (SA_{total}), percent paint damage (%PD) and required current density (i_{required} , table 16), I_{anode} being the delivered current per sacrificial anode based on the anode type and the driving voltage and N the number of anodes. In the calculation of I_{anode} , ASA is the useful surface area of the anode (i.e. the surface of the top and four sides while the underside is not an exposed area if in tight contact with the substrate), E is the driving potential in volts DC (table 17), K a constant with a value of 0.439 if the anode area is expressed in square meters.

Type of tank	Cargo carried	Recommended current density
Upper wing tanks Peak tanks	Salt water	130 mA/m ²
Segregated ballast tanks Deep tanks Cargo ballast (Spirit tankers)	Salt water (Petroleum products/salt water)	110 mA/m ²
Double bottom tanks Cargo ballast	Salt water Crude oil/salt water	90 mA/m ²

Table 16: Recommended current density (I-required) for different uncoated tanks and cargoes (after Botha 2000)

E	Sacrificial Anode Type	
Substrate Material	Zinc, Aluminium	Magnesium
Steel	0.45 V	1.0 V
Bronze, Copper, Nickel	0.80 V	1.35 V

Table 17: Value of E for different types of sacrificial anodes and tank alloys (after SSC-390, 1996)

The application of anodes presents a few distinct disadvantages. Firstly, there is a significant recurrent cost needed for the procurement and installation of the anodes in the tanks. For example, for a Panamax bulk carrier the cost comes down to approximately \$500,000 (McNulty, 2007) which is not even a onetime cost, since a sacrificial anode is designed to last five years. Also, the use of anodes is literally ponderous. For example, an Ultra Large Crude Carrier (ULCC) can have 67 ton zinc on board as cathodic protection system (McNulty, 2007). This means that on each and every voyage, 67 ton less can be loaded as useful cargo.

Moreover, the dissolution of heavy metals, that are subsequently discharged into the marine environment upon release of the ballast content of the tank, cause extra pressure on the marine ecosystems (Bird, 1996 & Gardiner, 2003).

On top of that, there are some authors that question the effectiveness of the sacrificial anodes in situ, i.e. installed in a tank, instead of under lab or pilot test conditions. For example, Bertolini (Bertolini, 2002) notes: "sacrificial anodes may be more effective in preventing corrosion initiation (i.e. in providing cathodic prevention) than in controlling ongoing pitting corrosion (i.e. in guaranteeing cathodic protection)." As indeed many studies occur under controlled lab conditions, and only few address actual conditions in a ballast tank (Gudze, 2008) we have used the data from our ongoing in situ investigations (Verstraelen, 2009) to offer additional insights on whether the presence of a sacrificial anode has a measurable impact on the life expectancy of a merchant ship's ballast tank.

9.2 Materials and methods

Data were collected on a random set of 100 ships, following the protocol outlined in Verstraelen (Verstraelen, 2009). To preserve confidentiality of the collaborating traders and ships, the identity of the ships in this study cannot be divulged. Corrosion was estimated using the method and the corrosion index (CI) described by Verstraelen (Verstraelen, 2009).

To give a general overview of the corrosion in the tanks that were investigated in this study, the data were analyzed initially using a service life model that is based on two assumptions: an initiation time and a propagation time. A common linear model relation for the propagation time is used, allowing for a rapid and accurate assessment of the kinetics of structural failure of the average ballast tank (Verstraelen, 2009). Usage of the linear model in the time frame we are operating in, also allows for the use of classical inferential statistics, such as a straightforward ANOVA and statistical analysis was performed in EXCEL using the built-in formulae and algorithms for the calculation of the Student t-value, the Shapiro-Wilk test for normality and of ANOVA. The weak point of this approach is that the estimation of the initiation time can be discussed. In the analysis the linear relationship was assumed for all observations and the initiation time is determined by the intercept with the time axis.

Of course, as the measured CI is a percentage, with a theoretical range between 0 and 100, classic linear regression methods are not completely sufficient as their predictions are not limited to this allowable range. Also, since severely corroded ships are being taken out of the population, there is a bias towards structurally better ships in the higher age ranges, causing also a deviation of a straight line (as the service model generates). Therefore we opted for an approach that is complementary to the service model approach, by transforming the data using a generalized

linear model (Faraway, 2006 & Wood, 2006). This transformation was done by way of the logit-function:

$$\text{logit}(CI) = \ln\left(\frac{CI}{100 - CI}\right) \quad (\text{Equation 12})$$

The statistical analysis and the graphics were done with the open source software package R (Wickham, 2009).

9.3 Results

In the population of ships under scrutiny in the present study, 35% of the ballast tanks were outfitted with sacrificial anodes. These tanks were further divided into three ballast categories: always dry (less than 3% of the time completely or even partly filled), alternatively dry/wet, and always wet (more than 75% of the time partly or completely filled with water). 74% of the tanks were alternatively dry/wet, 21% were always immersed and 5% were always dry (figure 87). When present, the anodes had been installed at the time of the ship's construction.

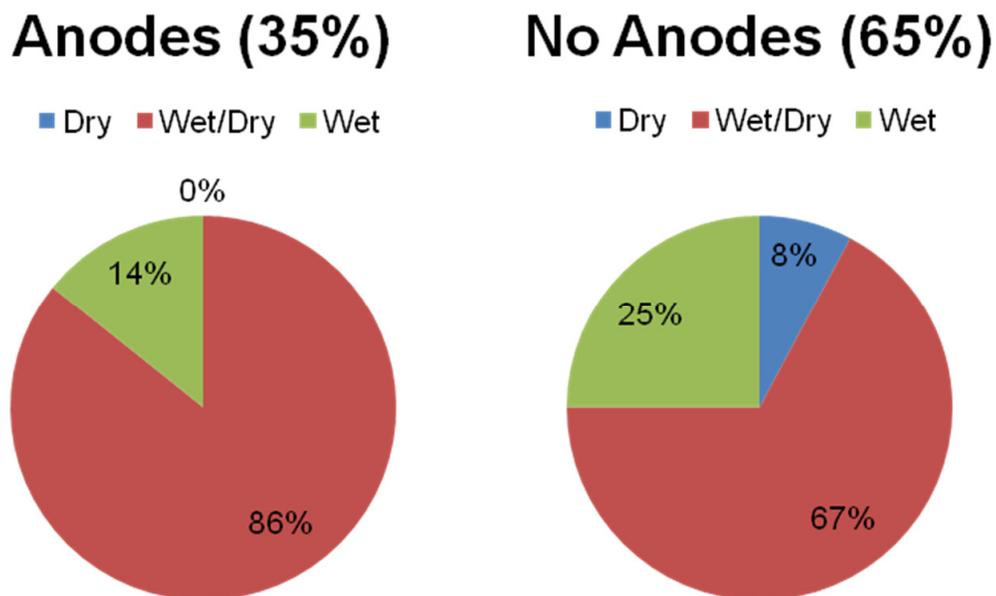


Figure 87: Distribution of anodes and ballast regime among the ships represented in our data set

To analyze whether the presence of anodes have an impact on the degree of corrosion a ship has sustained, we have compared the degree of corrosion of every ship to the average degree of corrosion after a certain time period. The progress of corrosion in ships outfitted with anodes or without anodes was analysed by plotting the level of corrosion (expressed

in terms of our CI) as a function of the age of the ships we investigated. Following the linear service life model using a linear regression on almost all data, as explained later, we obtain $CI = 1.6817t - 7.1449$ where t is the time after coating expressed in years. We note that coating breakdown starts after approximately 4 years, with an average of 1.7% per year. After 10 years, the ballast tank condition passes from "GOOD" to "FAIR" (sensu Verstraelen et al. 2009a and references quoted therein). After 22 years, the tank condition is categorized as "POOR" (figure 88A). The logit transformed data have been shown in figure 88B for comparison.

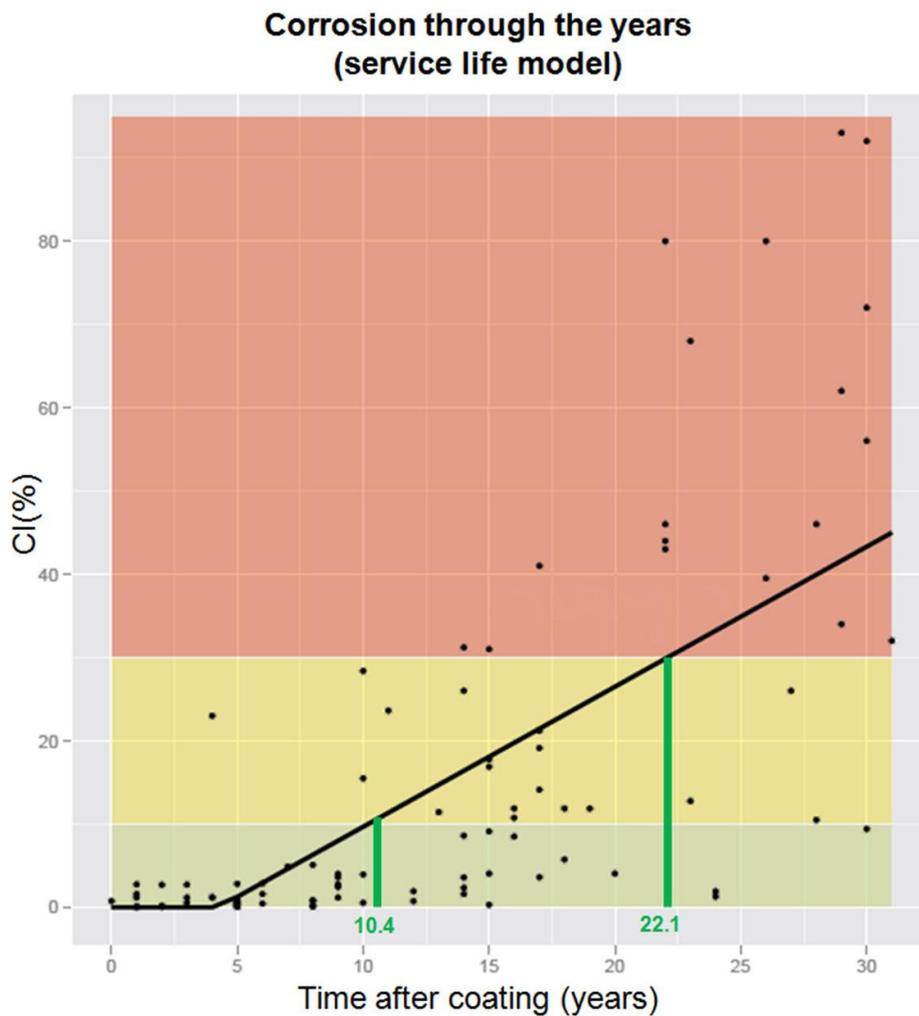


Figure 88A

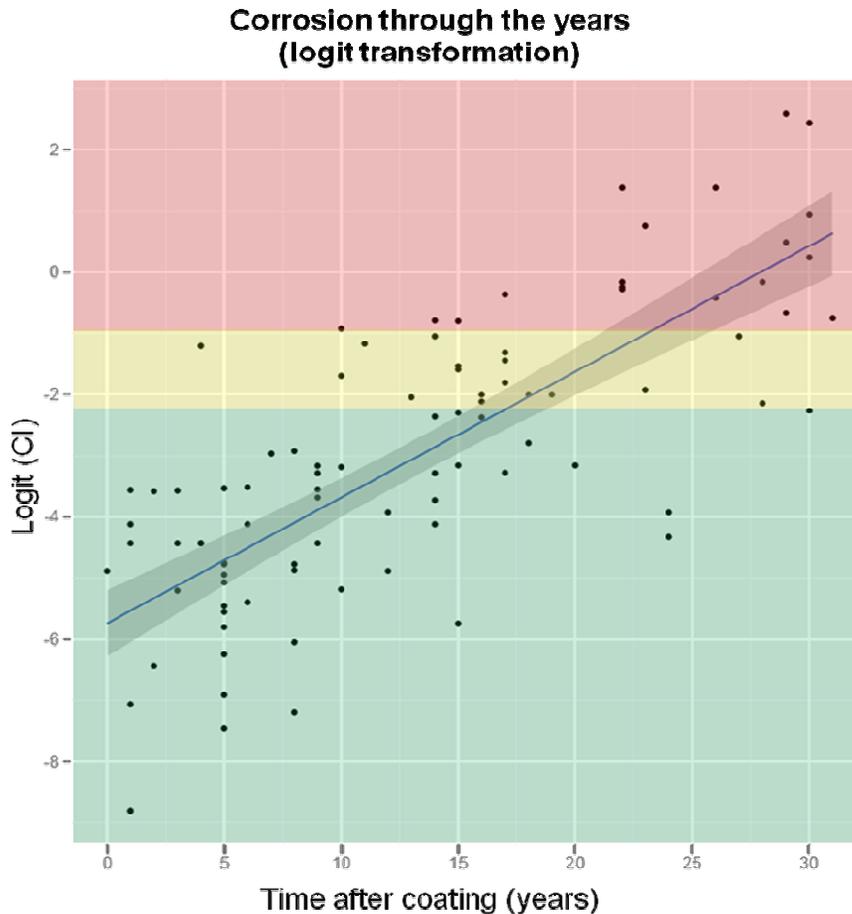


Figure 88B

Figure 88: Time dependence of the corrosion progression. A. Regression through the raw data based upon the service life model. B. Generalised linear model after logit transformation of the raw data; the grey zones indicating the 95% confidentiality intervals. The colours in both diagrams indicate the condition of the tank, ships in the green zone being "good", in the yellow zone "fair", and in the red zone "poor", according to the classification by IACS (2006)

From the rest of the analysis it will be clear that the logit transformed data provide more solid statistical ground for conclusions, whereas the service life model and its simpler linear regression, performed on the non-transformed data, allow for easier calculations. Here, we use the logit model to back up any conclusions from the service life model.

To allow for a better comprehension of the mechanism behind the data, the tanks were distinguished according to the presence or absence of an anode, and according to the ballast regime (see also figure 87). For each ship, the difference was determined between the predicted degree of corrosion after a certain period of time, and the actual corrosion that was observed. The main assumption in this approach to guarantee the validity

of the ANOVA is that these differences follow a normal distribution. Based on a Shapiro-Wilk test ($P=0.07$), the null hypothesis of a normal distribution could not be rejected (data not shown). In the category always dry, there were only 5 ships available (all from ships without a sacrificial anode), hence this category was excluded from further analysis. The ANOVA indicated as well that there is no significant difference between the different categories ($P=0.44$). The average differences (and their standard errors) are represented in figure 89.

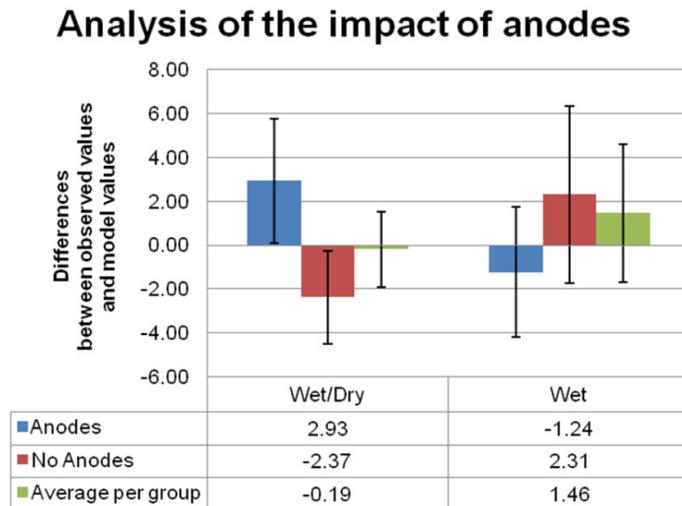


Figure 89: Average difference between observed and calculated CI (calculation based upon the linear regression of figure 88A) for ships with a wet/dry and a continuously wet ballast regime, in ships without (blue) and with anodes (red) or of the whole population (green). Bars indicate standard error, SD/\sqrt{n} , n depends on the condition (see figure 87)

In order to check the inference from the service life model we used the logit transformation for the data on tanks with or without anodes, and performed an analysis on both classes (figure 90). The grey zones surrounding each of the trend lines denote the 5% confidentiality interval, allowing for a statistical inference analysis of the data. The overlapping of these zones, along the entire length of the curve, indicates that there is no significant difference in terms of corrosion progression between tanks that are equipped with anodes and tanks that are not. If one makes abstraction of these confidentiality intervals, the data even suggest that tanks without anodes are performing slightly better than tanks without.

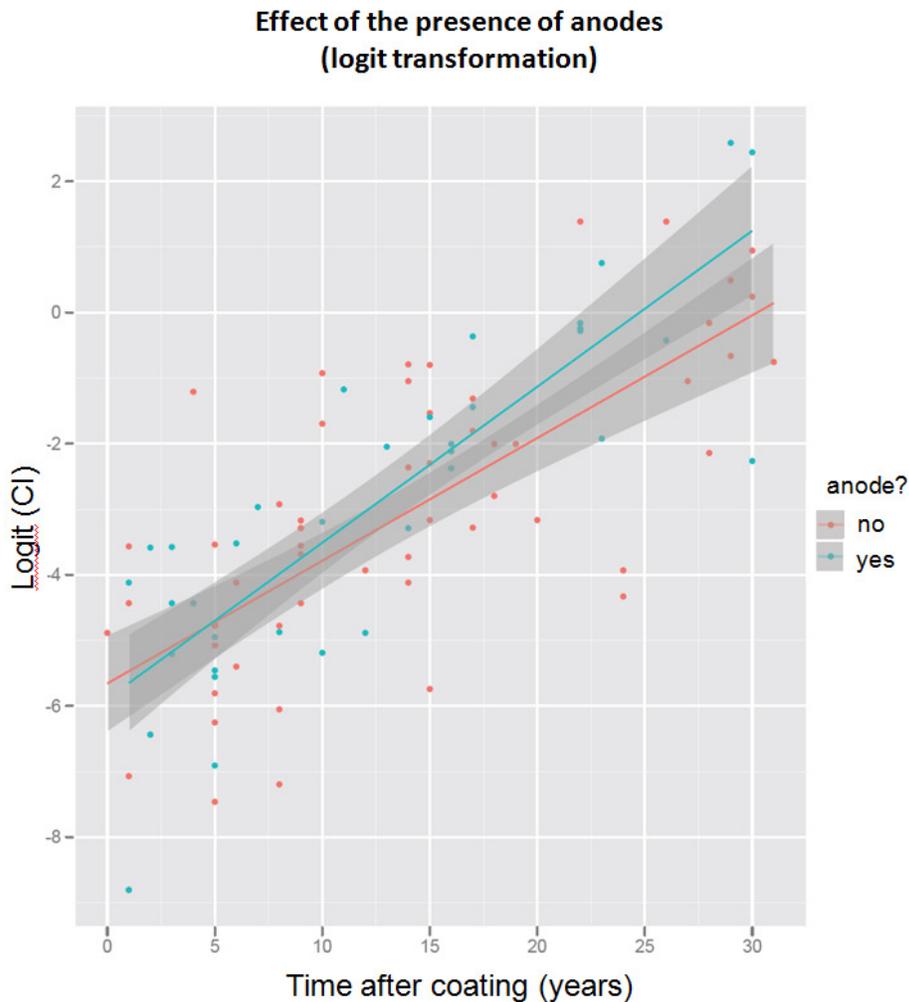


Figure 90: Linear regression through the data separated according to the presence of a sacrificial anode (orange dots and line: anodes absent, blue dots and line: anodes present) after logit transformation; the grey zones indicating the 95% confidentiality intervals.

9.4 Discussion

In our study, we have attempted to assess the effect of sacrificial anodes on the condition of a ship by analyzing the level of corrosion in different ships, each after a different period of active duty. That this is a valid approach in itself is debated elsewhere (De Baere, 2010). During these inspections, anodes were encountered in one third of the tanks; however, most of the time it was evident that they were not or hardly working. This a priori possibly subjective impression has been replaced now with a solid analysis of the observations, leading to the conclusion that, whatever use sacrificial anodes have in other circumstances, they fail to prevent or reduce corrosion in the ballast tanks of merchant ships. This paradox at

first sight is easy to explain if one looks beyond the physical principle to the practical limitations of the usage of sacrificial anodes.

To start with, while the total quantity of anodes required is fairly easy to calculate, one should note that several of these parameters are changing through time, diminishing the effectiveness of the original design, how well thought out it might have been upon construction. For example, the percentage of damaged coating surface must be taken into account in the equations (Equation 10) since this area is changing over time, the quantity of anodes should be recalculated at regular intervals. And there is more. IMO resolution A.798(19) (IMO, 1995) requires that when designing the cathodic protection system the ballast frequency, the resistivity and the temperature of the sea water should be taken into account. However, the resistivity of the ballast water will vary due to world wide variations in climate. Generally, 25 Ω .cm is a good approximation in European and Scandinavian waters while 15-20 Ω .cm should be applied in Middle-Eastern and Far-Eastern waters (Emirates techno casting, 2009 & NACE, 2007). This parameter is rather difficult to take into account since ships are sailing worldwide during all seasons, making seawater resistivity an ever changing parameter.

Moreover, the quantity of anodes installed in the tanks must be well determined to provide a good coverage (SSC, 1996). However, in practice, as evident during our in- situ inspections, we noted that the anodes were often distributed indiscriminately in the tanks. Undoubtedly the required quantity was present but no logical pattern in the anode distribution could be discovered. If an anode became detached, it was frequently not refitted or replaced till the next dry dock, maybe years later.

Furthermore sacrificial anodes work only when immersed in an electrolyte. Only at that moment the anode is sacrificed in favour of the exposed steel. Anodes should, as a result of this theory, be more efficient in tanks that are most of the time filled with ballast water, which might not permanently be achieved in a ballast water tank. However, according to MCA (MCA, 1999) and IACS (IACS, 2006), cathodic protection by sacrificial anodes is only effective when the metallic surface is immersed for a longer period of time (a day or more). MGDuff (MGDuff, 2009), a major supplier of sacrificial anodes, requires that for testing purposes the ballast water should have a relative density of 1.025 (the density of sea water) and should have been in the tank for at least 48 hours. This implicates that the anodes only become fully effective after 48 hours immersion.

Consequently anodes are not or hardly working on short sea trips and are only meaningful on longer trades.

In practice, however, ballast tanks on board of merchant ships are filled in function of the quantity and distribution of the cargo on board (see chapter 1). Expected sea state and condition together with the weather forecast will influence the quantity of ballast on board. Evidently, ballast tanks are alternately filled and emptied, and when they are filled they are not necessarily filled for 100%, leaving a void space above the ballast. On board of many ships it is even a standard rule not to fill up the ballast tanks completely as to prevent overflowing tanks (in order to have dry decks which allow for paint repair jobs). Our data analysis allows for this possibility by taking into account the ballast regime of the ships we inspected. Firstly, during the survey we noted that only 21% of the tanks is nearly always wet (a tank is considered "wet" if filled > 75% of the time). 84% of the tanks outfitted with anodes are sometimes dry and sometimes wet. Consequently, it is doubtful whether the sacrificial anodes in the majority of the ballast tanks are functional at all. Secondly, even in tanks that are continuously wet, there is no significant advantage to be noted linked to the presence of sacrificial anodes (figure 89).

Also, the structure of a ballast tank is extremely complex. On board of double hull ships all reinforcements have been shifted to the ballast tanks in order to obtain smooth-walled cargo compartments. An anode will normally protect surfaces in direct "line of sight": surfaces behind stiffeners, around corners, and inside pipes will not be adequately protected (SSC, 1996). Indeed, the key to a well functioning system is the proper location of all components on the complex hull geometry. In that case, anodes have to be installed in every cell of the structure to allow for a reasonable protection, which is physically nearly impossible and which is until now unheard of.

Another weak point of anodes is that they should be washed down regularly to remove sediments and other deposits. Ballast tanks are not provided with automatic washing installations. This washing down should be done by hand and therefore must be considered as unrealistic, considering the complex structure, the bad accessibility of the tank and a permanent shortage of crew on board.

Lastly, there are indications that an inadequate cathodic protection may be worse than doing nothing, as it may damage the coating itself, leaving the door wide open for faster corrosion induction. That means first and foremost that the compatibility of a coating system with a cathodic

protection system has to be proven (SSC, 1996 & Lohmann, 2007). Anodes must be placed clear of any overhanging stiffeners whenever possible, to aid the ionic flow around the anodes and prevent incorrect current flow. Wrongly sited anodes can result in severe blistering of the coating in their immediate vicinity (AMTEC, 2008). Improper design can cause overprotection, with resulting paint blistering and accelerated corrosion of some alloys or under-protection, with resulting structure corrosion or stray current corrosion of nearby structures (Hack, 1999).

An inaccurate design of cathodic protection systems may even result in bulkheads that are over-polarized, under-polarized, or contain regions of both, and either polarization extreme can be detrimental to the structure. Over-polarization will cause excess gas evolution and may lead to disbondment of coatings or embrittlement of high-strength materials; under-polarization can result in freely corroding material (Elsyca, 2009). Also, while in service, calcareous deposits can build up under the coating at any damaged area and can lift off the intact coating from the steel, thereby accelerating the rate of coating loss. These deposits are caused by alkali formed at the surface of a protected structure which reacts with bicarbonate ions present in sea water, thereby forming carbonate ions which, in turn, precipitate as insoluble calcium carbonate on the surface of the metal. This delamination is caused by a process called cathodic disbonding. Evidence of the unhappy symbiosis of sacrificial anodes and intact or nearly intact epoxy coating has been found in the ballast tanks of an ULCC, built 2002, during dry dock in February 2007 (figure 91).

In spite of all this, Kim et al. (Kim, 2007) suggest, after series of laboratory tests, that intact coatings are polarized by the anodes (below -0.79V vs. a saturated calomel electrode) just after several hours of immersion. The water penetrates through microscopic pores and capillary channels in the epoxy coating and reacts with the steel surface. The resulting cathodic reaction produces hydroxyl ions which penetrate the coating and are accumulated at coating/substrate interface. Based on this mechanism, they hypothesize that sacrificial anodes will cathodically improve the protection of the coated steel even when the coating is undamaged and so extend the service life of ships and offshore structures. We believe that under lab conditions, the hypotheses presented by this group are valuable data, useful to arrive at a better understanding of the chemistry involved in this complex system. However, our in situ findings demonstrate that in the end, sacrificial anodes have no positive effects on the protection of ballast tanks, and may even have negative consequences on the coating itself.



Figure 91: Effect of the presence of sacrificial anodes on the condition of the coating. Photos courtesy of Hempel.

9.5 Conclusions

A cathodic protection system only works when it is perfectly drafted. The minimum required current density for the cathodic protection to be effective has to take into account the geographic area, the coating breakdown and the seawater resistivity. On board of a merchant ship all of these parameters are constantly evolving rendering a well balanced protection system impossible. Too many unpredictable parameters are involved and the cathodic protection systems on hand lack flexibility to follow these variations. Indeed, ideal circumstances can be created in a laboratory but at sea, on board of a worldwide trading ship, subjected to ever changing circumstances this is not realistic. When the design circumstances are not met it is even possible that a negative reaction can be triggered.

After the whole series of in situ surveys, it is our conviction that anodes hardly slow down the corrosion progress in ballast tanks because only occasionally the cathodic protection system well balanced and positioned. This study suggests that, unless design and installation criteria are met and followed up, it may be more economical to abandon the use of sacrificial anodes in favour of a an alternative system.

9.6 Remark

The text of chapter 9 is literally the text as presented to Materials Performance in December 2009 for review, this in accordance with the preliminary remark of page 5. The article triggered a lot of opposite reactions especially from parties involved with the installation of sacrificial anodes claiming that the use of anodes is effective and well proven. After more than a year of mailing and writing we are still convinced that our research is sound and that anodes in ballast tanks are only useful if the cathodic protection system is well balanced and maintained and evolves in function of the condition of tank and coating.

However, the same conclusions were presented by us at the Ship Structure Symposium during the NACE corrosion conference from 13-17 march 2011. Paper 11419, In situ study of the parameters quantifying the corrosion in ballast tanks and an evaluation of improving alternatives, by De Baere et al. was published in the conference papers after extensive review by the world most renowned corrosion specialists.

We quote the conclusion regarding the use of sacrificial anodes.

Contrary to what could be predicted from the electrochemistry of a sacrificial anode system, the data, gathered during in situ visits of at random selected ballast tanks, presented in this article, throw some doubt on the reliability of such anodes. We do not question the efficiency of sacrificial anodes in ballast tanks if properly installed and maintained. Our visual observations, supported by the statistical interpretation of the data gathered do not show any significant advantage of the use of these anodes. Most probably this is caused by the specific environment- and construction-related characteristics of a ballast tank. Ballast tanks, especially on board of double hull ships are becoming more and more complex making cathodic protection increasingly difficult. Therefore, an intelligent construction and efficient coating application at the ship building yard seems to be useful better solution than the application of anodes.

No IMO or IACS regulation imposes the use of sacrificial anodes inside ballast tanks. Consequently, flag state or classification societies do not conduct initial or regular inspections. Since there are no rules and no inspection system a lot of liberty exists when installing the anodic protection system on board.

In June 2011, a modified version of the text of Chapter 9 was submitted to the journal Nature for review and maybe publication.

10. The cost of corrosion

10 The cost of corrosion



Figure 92: Typical Panamax tanker (Pennykall, 2007)

10.1 Introduction

Corrosion is a major cause of marine structure failures. Due to loss of material the scantlings are influenced and this results in diminishing of structural strength. Finally it leads to fatigue failure and stress corrosion cracking.

Corrosion is expensive. For example, the annual corrosion-related costs of the U.S. marine shipping industry are estimated at \$ 2.7 billion. This cost is divided into cost associated with new construction (\$1.12 billion), with maintenance and repairs (\$ 810 million), and with corrosion-related downtime (\$ 785 million)(Federal Highway Administration, 2002).

Statistics for ship hulls show that 90 % of ship failures are attributed to corrosion (Melchers, 1999). Localized corrosion is among the major types of physical defects found largely on ship structures. The areas of the ship

most susceptible to corrosion are the ballast tanks owing to the contact with seawater, humidity, and salty environment when empty.

The quantity of corrosion in ballast tanks is a decisive factor for ending the economic life of the ship and sending her to the scrap yard. To be able to make a semi-quantitative assessment of the tanks during regular inspections, an internationally accepted scale is in use, in accordance with IACS specifications. This scale consists out of three levels: "GOOD", "FAIR" and "POOR", as detailed in chapter 4. The condition of the ballast tanks should be "GOOD" at all times. "FAIR" will invoke expensive yearly inspections and "POOR" is a situation that should never exist and that could endanger the safety of ship, cargo and crew (ABS, 2007). For research purposes, one may equally rely on the CI presented in chapter 4 of this dissertation.

Today, ship's tanks are constructed in grade A⁴⁴ steel and protected with a standard epoxy coating⁴⁵ and sacrificial zinc anodes. Such a construction has been applied without significant alterations for many years. However, the goal of this study is to compare this construction method with some feasible alternatives through a cash flow analysis. As such, the impact of any structural investments can be investigated in the conceptual stage of the vessel. Important elements in such an analysis are the design of the tank and the selection of appropriate construction material.

The model selected for this study is a Panamax tanker of approximately 75,000 MT deadweight or DWT⁴⁶, a length overall or LOA⁴⁷ of 228 m, and a beam of 32.2 m.

Panamax tankers are ships constructed on the size limits for ships travelling through the Panama Canal. The maximum LOA of the ship is determined by the usable length of the lock being 304.8m. The maximum draft (12.04 m in tropical fresh water) is limited by the shallowest depth at the south sill of the Pedro Miguel locks and the maximum air draft of 57.91 (at any state of the tide) is defined by the clearance under the Bridge of the America's at Balboa. The maximum width over outer surface

⁴⁴ Grade A steel is ordinary ship construction steel following Lloyds Register requirements

⁴⁵ Epoxy coating is the standard coating used in ballast tanks since IMO PSPC (2006).

⁴⁶ DWT = the deadweight of a vessel is the maximum weight of the cargo, crew, stores and bunkers that it can carry when loaded so that it settles in the seawater to the Plimsoll line. This is also measurable by the weight of the water the vessel displaces when fully loaded less the displacement when it was unloaded.

⁴⁷ LOA = Length Overall = The total length of a ship's hull from the foremost to the aftermost points.

of the shell plating is 32.31 m. The deadweight of a Panamax ship varies between 50,000 and 80,000 DWT.

This model has been selected, because it is a very generic ship type. Panamax ships can be considered as a good representation of the medium size merchant ship and this category represents approximately 48 % of the world fleet.

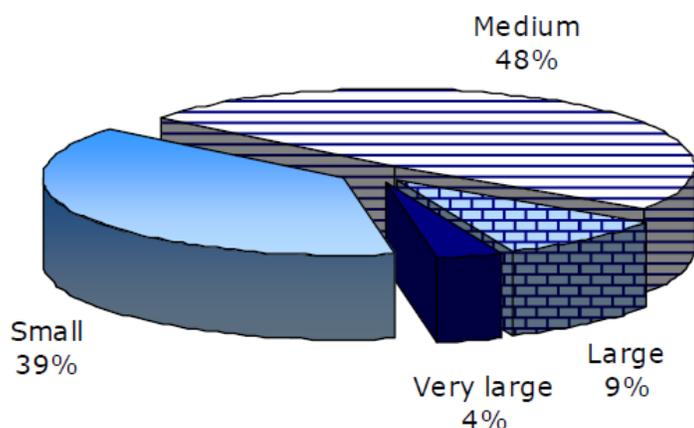


Figure 93: World fleet: total number of ships, by size – 2005 (European Maritime Safety Agency, 2005)

It is our objective to calculate the cost of corrosion in ballast tanks only. In order to avoid that other ship's parameters are affecting these estimations we limit our assessments to the size and weight of the ballast tanks only. Starting point is the surface of the ballast tanks set at 51,000m² (Mc Nulty, 2008).

We suppose that the ship has been built in China and dry docks in Bahrain due to the availability of recent and complete data.

10.2 Objective

The purpose is to compare 4 different cases of ballast tank construction and equipment within the possibilities of current available techniques and materials in order to reduce the cost.

Guideline for the selection of the different alternatives was a text published by Safinah "Equivalent" Ballast Tank Protection" published in March 2009.

Case I: This is a typical tank as constructed today in ordinary grade A steel, 14 mm thickness, coated with a standard PSPC⁴⁸ coating and equipped with zinc sacrificial anodes⁴⁹. This tank remains intact for approximately 5 years but subsequently the coating starts to degrade and corrosion appears requiring steel replacement and paint repair in function of the time. The anodes have to be replaced every 5 years.

Case II: In Case II the core element is corrosion allowance. The corrosion allowance is the diminution of steel allowable due to corrosion measured over a specific dimension of the element. For a ship this is laid down by her classification society. This means that in the lifespan of a ship a certain quantity of corrosion is tolerable without endangering the structural integrity of the ship. In practice (rule of thumb) steel will be replaced, in dry dock, when its thickness has been reduced to 80 % of the initial value. The present corrosion allowances of even more conservative classification societies are marginally adequate for a 20-year design life vessel (Grastos & Zachariadis, 2010).

In Case II, the corrosion allowance has been doubled from 3 to 6 mm. By doing so the construction material becomes so thick that a replacement is never necessary during the total economical life of the ship. A Panamax tanker requires approximately 1,200 ton more steel to reach the 25 years life time goal (own calculation). This figure corresponds reasonably well with the value of 800 ton for a CSR Panamax ship presented by Grastos and Zachariadis (2010).

Consequently the ship's weight is increased and so the cargo carrying capacity is reduced. Case II contradicts the present "carry cargo, no steel" attitude of the ship yards. As in Case I, the anodes have to be replaced every 5 years. A positive element is that the time in dry dock will be reduced since no more steel replacement is necessary.

Similar to Case I a standard PSPC coating is applied.

Case III: In Case III, ships receive a TSCF₂₅⁵⁰ coating on top of 14 mm grade A steel. The lifetime of this coating is extended to the economical lifetime of the ship by a better preparation of the substrate, improved application conditions and an increased coating thickness. Consequently steel replacement is non-existing and the coating repair is reduced. Since

⁴⁸ PSPC: Performance Standard for Protective Coatings, IMO 2006.

⁴⁹ Sacrificial anodes: Metallic anode used in cathodic protection of ballast tanks

⁵⁰ TSCF: Tanker structure cooperative forum provides a platform for technical dialogue on structural aspects of tankers. This forum proposed in "Guidelines for Ballast Tank Coating Systems and Surface Preparation", 2002 a coating system with a lifetime expectancy of 25 years.

the surface attacked by corrosion is reduced, so will be the consumption of the sacrificial anodes. The anodes will be replaced only once every 10 years.

Case IV: The tanks are constructed in corrosion resistant steel⁵¹ and painted with an esthetical white coating because IMO PSPC requires that all ballast tanks are to be coated with a clear epoxy coating independent the material of construction. Coating repair remains necessary, although reduced. Anodes become redundant.

The economical life of the ship is set at 25 years. Afterwards the ship is sold for scrap iron.

The following table gives an overview of the comparative criteria.

	Case I	Case II	Case III	Case IV
Steel	Grade A	Grade A	Grade A	Corrosion resistant
Paint system	IMO PSPC ₁₅	IMO PSPC ₁₅	TSCF ₂₅	1 coat white epoxy
Thickness	320µm	320µm	350µm	160µm
Paint quality	Pure epoxy	Pure epoxy	Pure epoxy	Pure epoxy
Anodes	Yes	Yes	Yes	No
Replacement of the anodes	Every 5 years	Every 5 years	Every 10 years	NA
Coating repair	Yes	Yes	Yes	Yes
Increased scantlings	No	Yes	No	No
Steel replacement	Yes	NA	NA	NA

Table 18: Construction, equipment and maintenance criteria of the different tank types

⁵¹ CRS: Corrosion Resistant Steel

10.3 Calculation of the lightweight of the tanks

As mentioned before the tanks have a surface of 51,000 m². We suppose that plates of 14 mm thickness have been used and that the density of the steel is 7.8 ton/m³. From these data, the weight of the tanks can be calculated to be 5,569.2 ton. This weight is applicable for Cases I, III and IV.

Regarding Case II tanks, the corrosion allowance was doubled increasing the thickness of the plate from 14 mm to 17 mm. Consequently, the weight of the tank becomes 6,762.6 ton.

nr	Item	value	Source	Abbrev.
1	Surface ballast tanks	51,000 m ²	(http://www.nei-marine.com/documents/VOS_Life_Cycle_Cost_Panamax.pdf)	OPP
2	Density steel	7.8 ton/m ³	http://hypertextbook.com/facts/2004/KarenSutherland.shtml	DENS
3	Plate thickness	14 mm	Own estimation	
4	Corrosion allowance	3 mm	IACS common structural rules for oil tankers and bulk carriers	CA
5	Lightweight Tank I, III & IV	5,569.2 ton	Own calculations	LWT _T
6	Lightweight Tank II	6,762.6 ton	Own calculations	LWT _{II}

Table 19: Parameters used to calculate the weight of the tanks (LWTT)

10.4 Initial investment

When calculating the initial investment, three parameters were taken into account.

1) Cost of the steel construction

- Constructions in grade A steel were estimated at 1,750 €/ton [CAN]
- Constructions in CRS⁵² were estimated at 2,275 €/ton [CNCRS]

2) Coating cost

- PSPC₁₅ costs 40 €/m² [PSPC₁₅]
- Coating CRS tanks 35 €/m² [CCRS]
- TSCF₂₅ costs 63 €/m² [TSCF₂₅]

3) Cost anodes

- The tanks are equipped with 325 sacrificial anodes of 22 kg each. Cost per piece including installation: 72 €/anode [IA]

nr	Item	value	Source	Abbrev.
1.	Initial coating PSPC ₁₅	40 €/m ²	Nei-marine PPT on alternatives for PSPC mentions 50 dollar per m2 (2008)	PSPC ₁₅
2.	Initial coating TSCF ₂₅	63 €/m ²	Personal communication IHC Netherlands	TSCF ₂₅
3.	Initial coating CRS	35 €/m ²	Own estimation	CCRS
4.	Number of anodes	325	(http://www.nei-marine.com/documents/VO_S_Life_Cycle_Cost_Panama_x.pdf)	A
5.	Initial installation anodes	72 €/anode	Each anode weighs 22kg à 2€/kg + 28€ installation cost (Bahrain 2007)	IA
6.	Grade A steel purchase price	500 €/ton*	e-mail ArcelorMittal 01/09/2010	AS
7.	CRS steel purchase price	650 €/ton	30% > grade A, POSCO, personal communication	CRS

⁵² CRS: Corrosion resistant steel

8.	Cost building grade A	new in	1,750 €/ton	Own estimation based on new building value of a panama tankers and the lightweight	CAN
9.	Cost building grade CRS	new in	2,275 €/ton	By analogy calculation retail price grade A steel (x 1,3)	CNCRS

Table 20: Parameters used to calculate the initial investment

* 500 €/ton seems very low. We did some further inquiries and came up with the following results.

01/02/2011 <http://www.alibaba.com/showroom/ship-construction-steel-plate.html> mentions ship construction plate at 550-1200 USD/ton (376.5-822 €/ton)

01/02/2011 [http://steelprices-china.com/news/index/2011/02/01/MjIyODA%3D/POSCO to hike SBQ plate price to Hyundai Heavy.html](http://steelprices-china.com/news/index/2011/02/01/MjIyODA%3D/POSCO%20to%20hike%20SBQ%20plate%20price%20to%20Hyundai%20Heavy.html) Japanese steelmakers offer prices of around USD 800 per ton FOB for their ship plates export under negotiation with the Korean shipbuilding companies. (550 €/ton)

11/05/2011 We contacted ArcelorMittal again to have an update on the price of ship construction steel grade A. They mentioned that the steel price was, since a few months, rising very steeply at 65% per year. On <http://www.meps.co.uk/EU%20price.htm> quarto plates are treated at 650 €/ton. This could rise to 750 €/ton in function of the steel treatment as mentioned on [http://www.arcelormittal.com/fce/repository/ Price%20lists/ EN hotrolledplates EUR.pdf](http://www.arcelormittal.com/fce/repository/Price%20lists/EN_hotrolledplates_EUR.pdf)

Since the market price of the grade A steel is changing so quickly it is a bit useless to try to keep up. We decided to maintain the price of 500 €/ton (correct at the time of writing of this chapter) and to include in the sensitivity study an extra margin considering this variability. However, we supposed that if the price of grade A varies, the price of CRS, steel repair work and scrap will vary to the same extent.

Taking into account above mentioned variables the initial investment can be calculated as follows.

Case I: Initial investment = $(LWT_T \times CAN) + (OPP \times PSC_{15}) + (A \times IA)$

This type of tank weighs 5,569.2 ton, has a surface to be coated of 51,000 m² and is equipped with 325 anodes. Multiplying these quantities with the respective unit prices⁵³ gives the following result.

Initial investment Case I = $(5,569.2 \times 1,750) + (51,000 \times 40) + (325 \times 72) = 11,809,500 \text{ €}$

Case II:

Initial investment = $(LWT_{TII} \times CAN) + (OPP \times PSC_{15}) + (A \times IA)$

This type weighs 6,762.6 ton, has a surface to be coated of 51.000 m² and is equipped with 325 anodes. Multiplying these quantities with the respective unit prices gives the following result.

Initial investment Case II = $(6,762.6 \times 1,750) + (51,000 \times 40) + (325 \times 72) = 13,897,950 \text{ €}$

Case III: Initial investment = $(LWT_T \times CAN) + (OPP \times TSCF_{25}) + (A \times IA)$

This type weighs 5,569.2 ton, has a surface to be coated of 51,000 m² with an improved coating system and is equipped with 325 anodes. Multiplying these quantities with the respective unit prices gives the following result.

Initial investment Case III = $(5,569.2 \times 1,750) + (51,000 \times 63) + (325 \times 72) = 12,982,500 \text{ €}$

Case IV: Initial investment = $(LWT_T \times CNCRS) + (OPP \times CCRS)$

This type weighs 5,569.2 ton, has a surface to be coated of 51.000 m² with ethical coating to satisfy IMO PSCP and no more anodes are provided. Multiplying these quantities with the respective unit prices gives the following result.

Initial investment Case IV = $(5,569.2 \times 2,275) + (51,000 \times 35) = 14,454,930 \text{ €}$

⁵³ See table 3

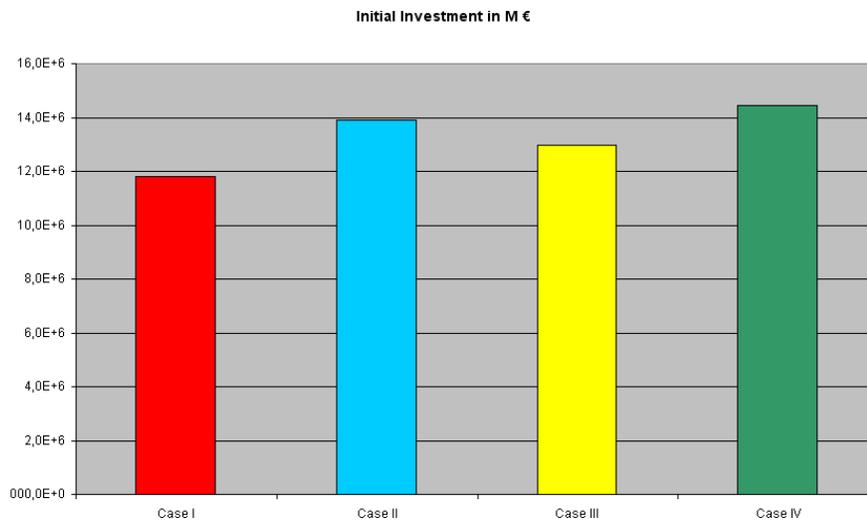


Figure 94: Initial investment in € (on Y-as)

10.5 Exploitation cost

The exploitation costs take five elements into account:

- Steel renewal cost
- Coating repair cost
- Cost to replace the anodes
- Cost of unavailability of the ship due to dry dock.
- Loss of cargo carrying capacity due to an increased lightweight⁵⁴ for Case II ships

Effective ship maintenance can only be carried out during dry docks. A ship has to visit dry dock 2 times every 5 years. These dry docks are not equally important. We suppose that that steel- and coating repair jobs are exclusively done during the principle docking every 5 years.

nr	Item	value	Source	Abbrev.
1	Repair PSPC ₁₅	61.35 €/m ²	George Terkels (ASR) + Rob Hoogenboom (Hempel), personal communication 54 €/m ² grit blasting + 4.85 €/m ² paint application + 2.5 €/m ² paint	RPSPC
2	Repair TSCF ₂₅	96.62 €/m ²	Own estimation	RTSCF

⁵⁴ LWT: Lightweight = weight of the empty ship/tank.

3	Replacement anodes	72 €/anode	Own estimation	RA
4	Replacement grade A steel	3,900 €/ton	Bahrain 2008	RAS
5	Replacement CRS steel	7,800 €/ton	Own estimation	RCRS
6	Scrap per ton grade A steel	325 €/ton	475 \$/ton China Jan. 2011	SCI
7	Scrap per ton CRS steel	325 €/ton	Own estimation	SCRS
8	Rental dry dock	2,885 €/day	Bahrain 2008 (LXBX0.5\$/dag)	CDD
9	Time Charter Equivalent Panamax tanker	15,514 €/day	http://www.mis.gr/main/docs/legacy/legacy-2010-34.pdf	TC

Table 21: Parameters used to calculate the exploitations costs

The cost of steel renewal, coating repair, the replacement of anodes and the rental cost of the dry dock are based on the price list of Bahrain ASRY dry docks of 2008. More recent prices were available from other dry dock facilities but the set of Bahrain was the only complete list for the purposes of this study. We chose to use Bahrain based upon this completeness.

10.5.1 Steel renewal cost

In 2006, Dr. Philippe Rigo from ANAST-Liège, Dr. Petri Varsta from Helsinki University and Dr. Vedran Zanic from the Zagreb University launched a European Project IMPROVE. The main objective of the IMPROVE project is to design 3 different types of next generation vessels by integrating different aspects of ship structural design into one formal framework and applying it. In the context of this IMPROVE project a generalized life cycle cost model has been developed.

Riadh Aloui, master student at the University of Liège, created equations 13 and 16, based on data extracted from the IMPROVE project.

The quantity of steel replaced during dry dock resulting from damage by corrosion, cracks and deformation but excluding accidents can be represented by the following regression.

$$\text{ASR/LWT} = 0.031e^{0.2982t} \quad (\text{Riadh Aloui, 2010}) \quad (\text{Equation 13})$$

ASR = the quantity of steel replaced per dry dock

LWT = lightweight of the ship

t = age of the ship

The data on which this regression is based was obtained from 3 shipping/managing companies who were willing to share the information regarding their past repair jobs. In total the details of 18 ships were used. The quantities steel replaced do not include repairs as a consequence of accidents.

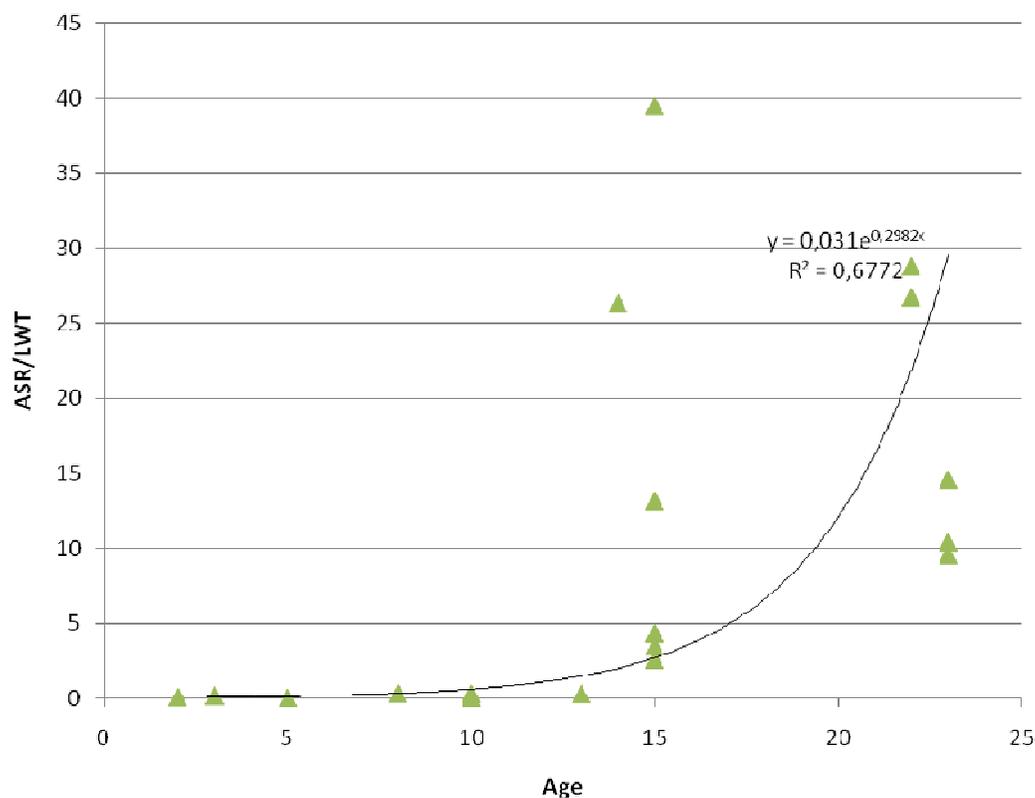


Figure 95: Quantity of steel (%) replaced per dry dock in function of the age of the ship (Riadh, 2010)

It is important to note that these ships were normally maintained and repairs have been carried out during every previous dry dock.

In the context of this study, aiming to determine the cost of corrosion, it is necessary to reduce the total quantity of steel work per dry dock to the steel replacement exclusively imposed by corrosion. Steel repair work can be a consequence of deformations, corrosion and cracks. In the context of

this chapter we are only interested in steel repair work inflicted by corrosion.

C1 is a factor quantifying the fraction of ASR/LWT caused exclusively by corrosion in function of the time (Kawano & Hirakata 2003):

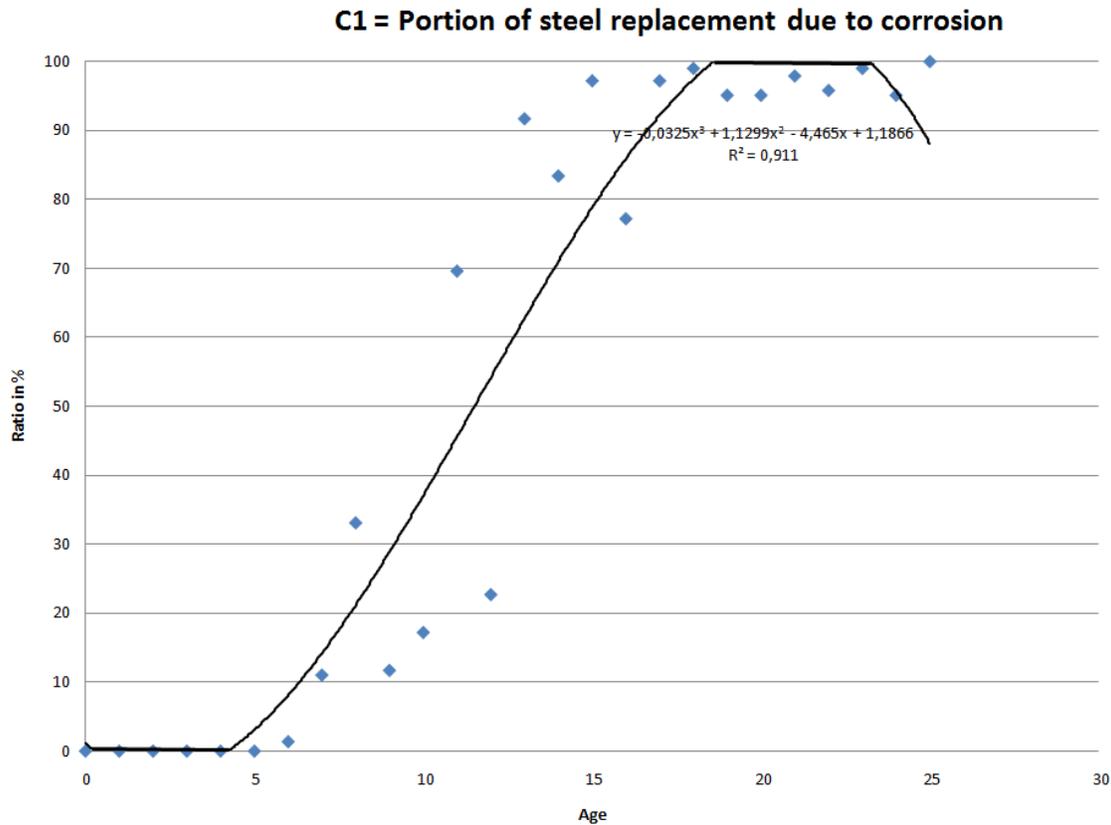


Figure 96: C1 in function of the age of the ship (graphical presentation of numerical data presented by Kawano & Hirakata 2003)

$$C1 = -0.0325t^3 + 1.1299t^2 - 4.465t + 1.1866 \quad (\text{Equation 14})$$

If we combine equations 13 and 14 we obtain the steel replacement quantity as a consequence of corrosion in function of the time.

Steel renewal cost = Equation 13 x Equation 14 x the lightweight of the tank⁵⁵ x unit cost of steel replacement per ton.

$$\text{Steel renewal cost} = (\text{ASR/LWT}) \times \text{LWT}_T \times C1 \times \text{RAS}$$

⁵⁵ For tank cases I, III and IV LWT_T is 5.569,2 ton for tank case II LWT_{III} is 6.762,6 ton

10.5.2 Coating repair

The surface to be recoated is calculated based on the equation:

$$CI = 1.6817t - 7.1449 \quad (\text{Equation 15})$$

CI = the corrosion index CI represents the surface of the coating damaged by corrosion in % and function of the time (chapter 4, 5).

This formula shows that a coating remains nearly intact during approximately the 4 initial years. Afterwards the paint degrades in a nearly linear fashion with approximately 1.7 % surface per year.

$$\text{Cost of recoating} = (1.6817t - 7.1449) \times 51,000 \times \text{RPSPC}$$

10.5.3 Replacement of anodes

Anodes have to be replaced every 5 year in normal conditions.

Due to the good performance of the TSCF₂₅ coating (Type III) we suppose that replacement is only required once every 10 years. Tanks built in corrosion resistant steel (Type IV) do not require any anodes at all.

$$\text{Cost of the anode replacement} = 325 \times 72 = 23,400 \text{ €}$$

10.5.4 Cost of unavailability of the ship due to dry dock

When a ship is in dry dock income is lost because the ship is not carrying any cargo. The following statistical regression is based on the duration of 41 dry dock events of 22 different ships ranging in age from 1 till 31years.

$$DLWT = 0.7721e^{0.0726t} \quad (\text{Riadh Aloui, 2010}) \quad (\text{Equation 16})$$

The formula gives the number of days spent in dry dock divided by the lightweight of the ship in function of the time. If this value is multiplied with the lightweight of the tank the average number of days in dry dock is obtained.

Again, factor C1 (Equation 14) is used to recalculate this number to the number of days in dry dock as a consequence of corrosion damage.

In Bahrain the dry dock rental cost per day is calculated by multiplying the length of the ship with the beam and with 0.4 €. For the reference tanker it comes to 2,885 €/day.

The total cost of unavailability is obtained by multiplying the final number of days (DLWT × LWT_T × C1) with Time Charter Equivalent and adding the cost of the dry dock per day.

$$\text{Dry dock cost} = (DLWT \times LWT_{\text{TorTII}} \times C1) \times (TC + CDD)$$

10.5.5 Loss of income due to increased lightweight as a consequence of the doubling of the corrosion allowance

This cost is only applicable on board of the Case II tankers.

The ship is chartered at a TC of 15,514 €/day. By increasing the corrosion allowance the lightweight is increased with 1,193.4 ton while the cargo carrying capacity is diminished with the same number. This loss is only applicable during loaded voyages. We suppose that the tanker is loaded 50% of the time (Mc Nulty, 2008).

Loss of income = $((15,514 \times 365) / 75,000) \times 1,193.4) / 2 = 45,051.7$ €/year

10.6 Residual value

After 25 years of service the ship is sold at the value of the scrap iron being 325 €/ton (China, Jan. 2011)

The tanks constructed in CRS are also scrapped at 325 €/ton because we do not believe that the higher concentrations of valuable alloys will influence the scrapping price.

The residual value is obtained by multiplying the lightweight of the tank with the scrap iron price.

10.7 Cash flow

To take the general and progressive increase in prices into account the costs and the residual value are inflated with an inflation rate⁵⁶ of 6 %.

The net present value or NPV is calculated with a discount rate⁵⁷ of 4 % and the dollar exchange rate is set at 1 \$ = 0.68473 € (26/04/2011).

The cash flow equals the initial investment + the operational costs through 25 years – the residual value when the ship sold for scrap.

In the following tables an overview is given of cash flow movements. In the first table the costs and the residual value are inflated with 6 % per year in second table a supplementary discount rate of 4 % is taken into account.

⁵⁶ Inflation rate: the rate of increase of a price index

⁵⁷ Discount rate: the percentage by which the value of a cash flow in a discounted cash flow (DCF) valuation is reduced for each time period by which it is removed from the present.

	Case I	Case II	Case III	Case IV
Initial Investment	11,809,500.00	13,897,950.00	12,982,500.00	14,454,930.00
Operational costs				
0	-	45,051.73	-	-
1	-	47,754.83	-	-
2	-	50,620.12	-	-
3	-	53,657.33	-	-
4	-	56,876.77	-	-
5	88,981.87	146,830.73	42,821.88	12,737.03
6	-	63,906.73	-	-
7	-	67,741.14	-	-
8	-	71,805.61	-	-
9	-	76,113.94	-	-
10	701,094.98	718,755.47	495,775.06	145,700.66
11	-	85,521.62	-	-
12	-	90,652.92	-	-
13	-	96,092.10	-	-
14	-	101,857.62	-	-
15	1,966,856.20	1,741,649.34	1,178,514.80	407,594.08
16	-	114,447.23	-	-
17	-	121,314.06	-	-
18	-	128,592.90	-	-
19	-	136,308.48	-	-
20	4,731,378.84	3,440,397.58	2,449,543.50	863,047.83
21	-	153,156.20	-	-
22	-	162,345.58	-	-
23	-	172,086.31	-	-
24	-	182,411.49	-	-
25	-	193,356.18	-	-
Total operational cost	7,488,311.90	8,319,304.00	4,166,655.24	1,429,079.60
Residual value	7,768,243.08	9,432,866.60	7,768,243.08	7,768,243.08

Table 22: Initial investments, operational costs and residual value inflated 6% per year

	Case I	Case II	Case III	Case IV
Initial Investment	11,809,500.00	13,897,950.00	12,982,500.00	14,454,930.00
Operational costs				
0	-	45,051.73	-	-
1	-	45,918.10	-	-
2	-	46,801.14	-	-
3	-	47,701.17	-	-
4	-	48,618.50	-	-
5	73,136.61	120,684.15	35,196.46	10,468.91
6	-	50,506.42	-	-
7	-	51,477.70	-	-
8	-	52,467.65	-	-
9	-	53,476.65	-	-
10	473,634.65	485,565.44	334,927.87	98,430.15
11	-	55,553.22	-	-
12	-	56,621.55	-	-
13	-	57,710.42	-	-
14	-	58,820.24	-	-
15	1,092,125.43	967,076.05	654,387.44	226,322.52
16	-	61,104.31	-	-
17	-	62,279.39	-	-
18	-	63,477.07	-	-
19	-	64,697.79	-	-
20	2,159,339.54	1,570,152.54	1,117,939.68	393,883.76
21	-	67,210.09	-	-
22	-	68,502.59	-	-
23	-	69,819.95	-	-
24	-	71,162.64	-	-
25	-	72,531.15	-	-
Total operational cost	3,798,236.23	4,414,987.66	2,142,451.44	729,105.34
Initial investment	11,809,500.00	13,897,950.00	12,982,500.00	14,454,930.00
Residual value	2,913,998.50	3,538,426.76	2,913,998.50	2,913,998.50
Cash Flow	12,693,737.73	14,774,510.90	12,210,952.94	12,270,036.84

Table 23: Cash flow inflated with 6% and discounted with 4% per year

10.8 Results

Upon comparison of the cash flow results in table 23, it is obvious that the Case I, III and IV are very competitive. Case II, being the use of an thicker corrosion allowance is economically not the best of solutions. Expanded scantlings offers adequate protection against corrosion but the penalty of an increased lightweight and consequently the loss of cargo carrying capacity is simply too big. This conclusion confirms the statement of Johnny Eliasson at the Lloyd's List event conference, Prevention and Management of Marine Corrosion, London 2003, *"It is possible to build ships with such thick steel that even with free corrosion taking place the ship would have enough strength left to perform its designed service life. It is generally agreed today that this is no longer a cost efficient way to build and operate ships."*

However, the horizon of the future ship owner has broadened. A few years ago the classic combination of grade A steel protected with a PSPC₁₅ system coating and backed up with sacrificial anodes would not have been questioned. This study shows that it is may be worthwhile to take alternatives III and IV into consideration.

As we will show further on in the sensitivity analysis a lot of parameters, technical and financial, are capable of affecting which case is most beneficial.

The data used in this model are an approximation of reality. They provide a platform to compare the different cases and should not be considered as true costs. Huge differences exist and prices vary in function of geographical location, time and availability.

We should also bear in mind that Case III and IV are new and unproven. For example the results of this study rest upon the basic assumption that corrosion resistant steel lives up to the promised characteristics. At this moment these steel varieties are in an experimental phase and the exact features still remain to be established.

Additionally the exact retail price is unknown at present. The estimations used in this study are indicative and only based on the value of the composing alloy elements. It is almost certainly that when the demand for this product increases, the retail price will follow.

Also, the performance of TSCF₂₅ is questioned by certain shipyards. A Dutch shipyard mentioned as follows: *"The wish to reduce and eventually completely eliminate, the maintenance in ballast tanks is fully understandable. I am not aware of any independent scientific proof that the complete removal of the shop primer, the reduction of the allowable quantity of dust, a lowering of the maximal chloride pollution from 50 to 30mg/m², the increase of the layer thickness from 320 to 350 (90/10) micron and 3 full coats instead of 2 will result in an increase of life span of 67%."*

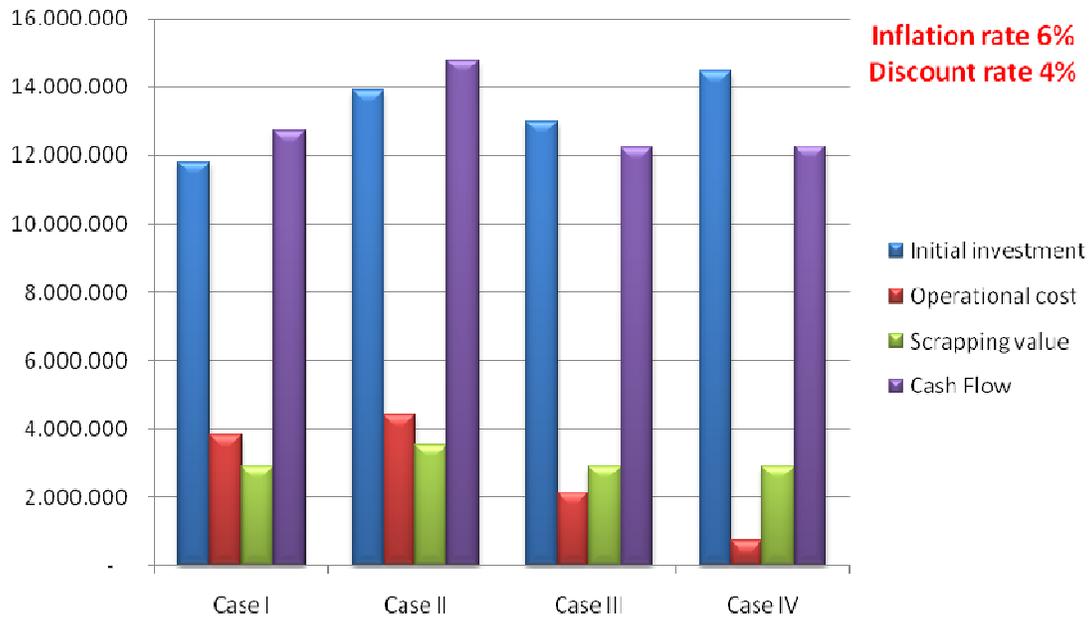


Figure 97: Initial investment, total operational cost, residual value and cash flow inflated and discounted (own work)

10.8.1 Sensitivity study of the different significant parameters to the “cost of corrosion” model

The purpose is to evaluate the relative importance of the most significant parameters and to study their ability to reverse the economical ranking as expressed by the cash flow.

As a reminder, the cash flow equals the sum of the initial investment plus the running costs minus the resell value of the ship. The comparison is made on the basis of a net present value taking into account a discount rate of 4% and an inflation rate of 6%. In a second part, the sensitivity of these rates will be investigated.

Sensitivity of the most important parameters of the standard model

Cost of anodes, cost of coating, time charter equivalent value, dry dock price, the scrapping value of the steel and the general steel price were selected as most significant. These prices were changed with 25% and 50% upward and downward and the result is represented by a change in percentage to the “standard condition”. A green color indicates that a rise in cost triggers a rise in cash flow. The red color indicates an inverse proportionality. The purple font color is used to highlight the element with the most important impact.

		Change in cash flow in % referring to the “standard” situation			
Parameter	Change	Case I	Case II	Case III	Case IV
Cash flow “standard” situation		100%	100%	100%	100%
Anodes (Installation + replacement)	+ 50%	+0.56%	+0.48%	+0.35%	NA
	+ 25%	+0.28%	+0.24%	+0.18%	NA
	-25%	-0.56%	-0.48%	-0.35%	NA
	- 50%	-0.28%	-0.24%	-0.18%	NA
Coating (PSPC15 & TCSF ₂₂ + coating on the CRS)	+ 50%	+17.39%	+14.94%	+20.82%	+9.39%
	+ 25%	+8.70%	+7.47%	+10.41%	+4.70%
	- 25%	-6.96%	-5.98%	-8.33%	-3.76%
	- 50%	-11.58%	-9.95%	-13.88%	-6.28%
TC (Time charter equivalent)	+ 50%	+2.78%	+6.28%	+0.72%	+0.72%
	+25%	+1.39%	+3.14%	+0.36%	+0.3%
	- 25%	-1.39%	-3.14%	-0.36%	-0.36%
	- 50%	-2.78%	-6.28%	-0.72%	-0.72%
Drydock (Cost per day)	+ 50%	+0.52%	+0.22%	+0.13%	+0.13%
	+ 25%	+0.26%	+0.11%	+0.07%	+0.07%
	- 25%	-0.26%	-0.11%	-0.07%	-0.07%
	- 50%	-0.52%	-0.22%	-0.13%	-0.13%
Scrapping value (Grade A = CRS)	+ 50%	-11.48%	-11.97%	-11.93%	-11.87%
	+ 25%	-5.74%	-5.99%	-5.97%	-5.94%
	- 25%	+5.74%	+5.99%	+5.97%	+5.94%
	- 50%	+11.48%	+11.97%	+11.93%	+11.87%
Steel price (grade A, CRS, steel repair and scrap)	+ 100%	+57.49%	+56.15%	+55.95%	+79.51%
	+ 50%	+28.75%	+28.08%	+27.98%	+39.76%
	+ 25%	+14.37%	+14.04%	+13.99%	+19.88%
	- 25%	-14.37%	-14.04%	-13.99%	-19.88%
	- 50%	-28.75%	-28.08%	-27.98%	-39.76%

Figure 98: Change in cash flow in % referring to the “standard” situation.

It is important to note that change in coating price has been applied equally to all coating methods. The same remark can be made for the change in steel price. Later on a difference will be made between the different coating systems and steel qualities.

The table shows that the influence of anodes and the cost per day of the dry dock is of little significance. The Time Charter Equivalent is of some importance for Case I, mainly influences Case II and is not substantial for Cases III and IV. The scrapping value has an equal influence on all of the models and is relatively unimportant.

The meaningful parameters are the coating cost and the steel price. These parameters are studied more extensively.

The steel price

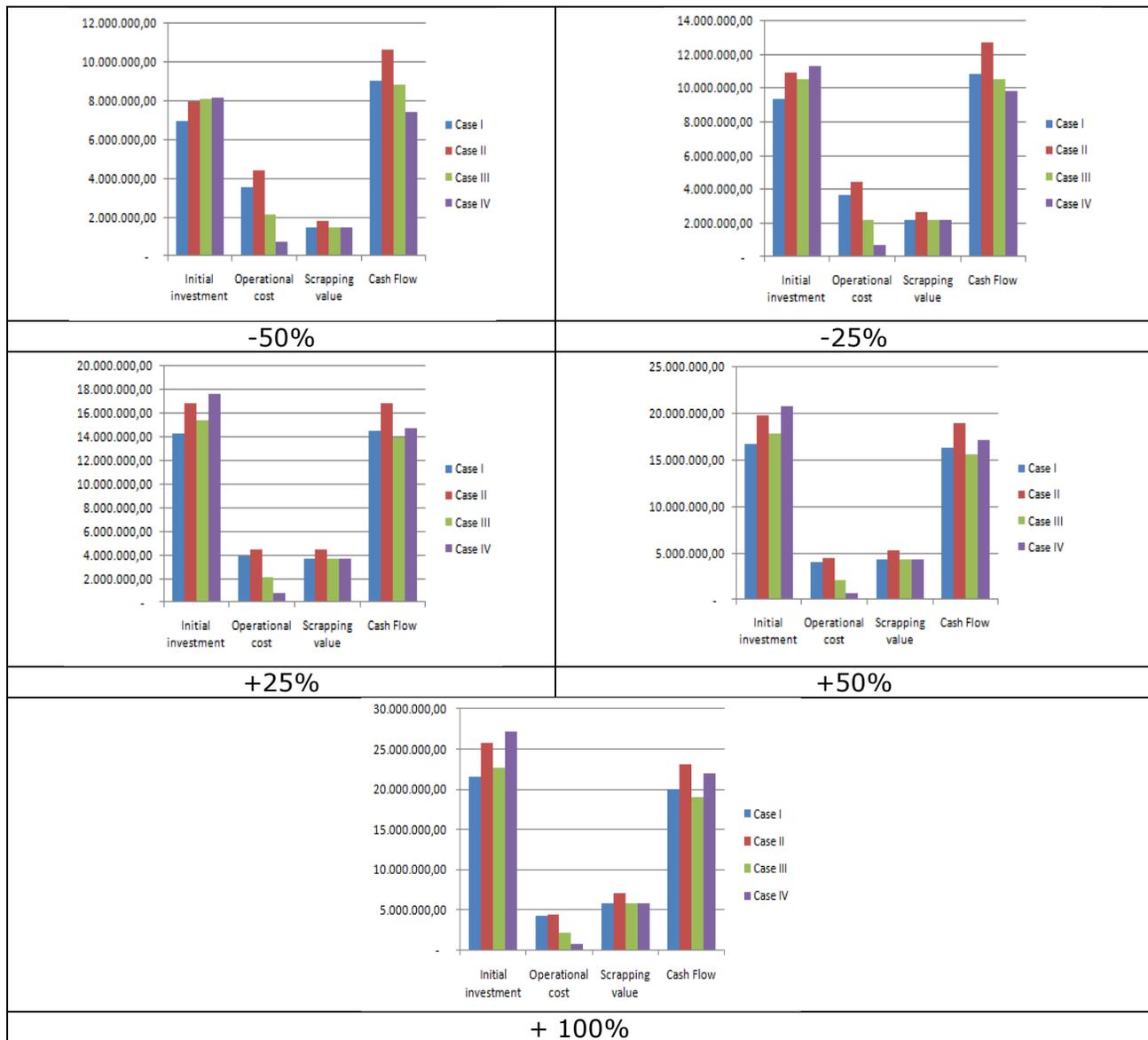


Figure 99: Influence of the steel price on the ranking of the Cases

Fig. 99 indicates that an increase in the steel price will have a clear-cut effect on the decision which type of ship is the most beneficial to produce. Given that such an increase can be expected for the near future, based upon the current steel price evolution (fig 100), it can be expected that Case IV will produce a higher cash flow, and therefore less favorable results in the long run. Cases I and III remain, competitive against each other.

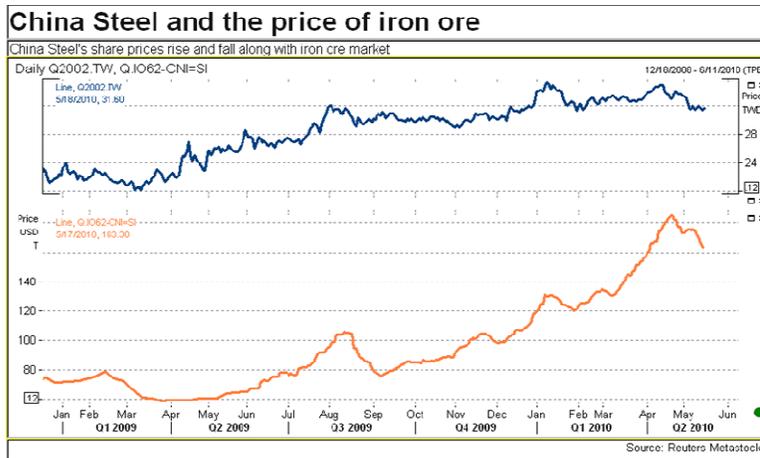


Figure 100: Evolution of the price of iron ore and steel in China (U.K. Reuters, 2010)

Coating

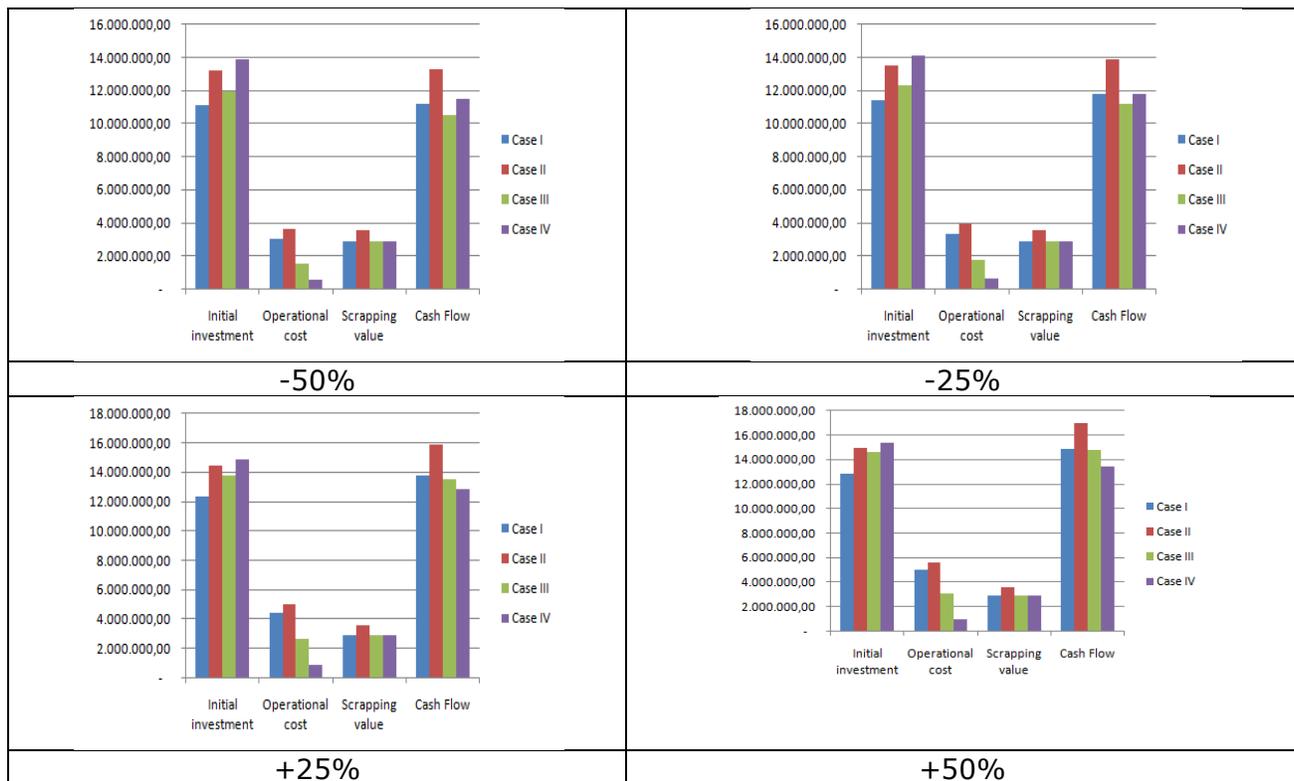


Figure 101: Influence of the coating cost on the ranking of the Cases

An increase of the cost related to the application and maintenance of a coating system favors Case IV, which has only an esthetical coat of paint, in relation to Cases I and III. It is at present unknown how coating prices will fluctuate in the future, especially because of the novelty of the TCSF₂₅ coating.

Relation price of CRS to grade A steel

In the reference model CRS is 1.3 times more expensive than grade A steel. The sensitivity of this parameter is tested by varying the prices of CRS between 1.0 and 1.6 times the prices of grade A.

The values in red indicate the reference model

	Cash Flow			
CRS = A	Case IV 9,346,206.84	Case III 12,210,952.94	Case I 12,693,737.73	Case II 14,774,510.90
CRS = 1.1 A	Case IV 10,320,816.84	Case III 12,210,952.94	Case I 12,693,737.73	Case II 14,774,510.90
CRS = 1.2 A	Case IV 11,295,426.84	Case III 12,210,952.94	Case I 12,693,737.73	Case II 14,774,510.90
CRS = 1.3 A	Case III 12,210,952.94	Case IV 12,270,036.84	Case I 12,693,737.73	Case II 14,774,510.90
CRS = 1.4 A	Case III 12,210,952.94	Case I 12,693,737.73	Case IV 13,244,646.84	Case II 14,774,510.90
CRS = 1.5 A	Case III 12,210,952.94	Case I 12,693,737.73	Case IV 14,219,256.84	Case II 14,774,510.90
CRS = 1.6 A	Case III 12,210,952.94	Case I 12,693,737.73	Case II 14,774,510.90	Case IV 15,193,866.84

Figure 102: Influence of price ratio CRS to grade A steel

The table shows that that if the price of CRS raises in respect to the price of grade A steel the use of long lasting coating systems is promoted and the use of CRS is discouraged.

Relation price of TCF₂₅ coating to PSCP₁₅ coating

In the economical model TSCF₂₅ coating is approx. 1.6 times more expensive than PSCP₁₅ coating. The sensitivity of this parameter is tested by varying the price of TSCF₂₅ between 1.0 and 2.0 times the price of PSCP₁₅ coating.

	Cash Flow			
TSCF ₂₅ = PSCP ₁₅	Case III 11,037,952.94	Case IV 12,270,036.84	Case I 12,693,737.73	Case II 14,774,510.90
TSCF ₂₅ = 1,2 PSCP ₁₅	Case III 11,445,952.94	Case IV 12,270,036.84	Case I 12,693,737.73	Case II 14,774,510.90
TSCF ₂₅ = 1,4 PSCP ₁₅	Case III 11,853,952.4	Case IV 12,270,036.84	Case I 12,693,737.73	Case II 14,774,510.90
TSCF ₂₅ = 1,575 PSCP ₁₅	Case III 12,210,952.94	Case IV 12,270,036.84	Case I 12,693,737.73	Case II 14,774,510.90
TSCF ₂₅ = 1,6 PSCP ₁₅	Case III 12,261,952.94	Case IV 12,270,036.84	Case I 12,693,737.73	Case II 14,774,510.90
TSCF ₂₅ = 1,8 PSCP ₁₅	Case IV 12,270,036.84	Case III 12,669,952.94	Case I 12,693,737,73	Case II 14,774,510.90
TSCF ₂₅ = 2,0 PSCP ₁₅	Case IV 12,270,036.84	Case I 12,693,737.73	Case III 13,077,952.94	Case II 14,774,510.90

Figure 103: Influence of the price ratio TSCF₂₅ to PSCP₁₅

The table shows that that if the price of TSCF₂₅ raises in respect to the price of PSCP₁₅ the use of long lasting coating systems is discouraged and the use of CRS is promoted.

The coating price is also a very sensitive element. Minimal changes is coating cost are able to influence the economical ranking of the cases.

Influence of the scrapping value of CRS

In the economical model the scrapping value of CRS is considered to be identical to the scrapping value of grade A steel. The sensitivity of this parameter is tested by varying the price of scrap CRS between 1 and 1.5 times the value of scrap grade A.

The value of scrap iron is varying very fast and is moreover dependent on the geographical location. We started from a value of 325 Euro/ton (China march 2011)

Scrapping value	Cash Flow			
	Case III	Case IV	Case I	Case II
CRS = grade A	12,210,952.94	12,270,036.84	12,693,737.73	14,774,510.90
CRS = 1,1 grade A	11,978,636.99	12,210,952.94	12,693,737.73	14,774,510.90
CRS = 1,2 grade A	11,687,237.14	12,210,952.94	12,693,737.73	14,774,510.90
CRS = 1,3 grade A	11,395,3837.29	12,210,952.94	12,693,737.73	14,774,510.90
CRS = 1,4 grade A	11,104,437.43	12,210,952.94	12,693,737.73	14,774,510.90
CRS = 1,5 grade A	10,813,037.58	12,210,952.94	12,693,737.73	14,774,510.90

Figure 104: Influence of the price ratio of scrap CRS to scrap grade A steel

Influence of the financial parameters

In this study a discount rate of 4% and an inflation rate of 6% are being used.

Influence of the discount rate

Discount rate of 6, 8 and 10% with a constant inflation rate of 6%

Discount rate	Cash Flow – inflation rate 6%			
4%	Case III 12,210,952.94	Case IV 12,270,036.84	Case I 12,693,737.73	Case II 14,774,510.90
6%	Case III 12,736,879.50	Case I 12,753,456.87	Case IV 13,174,993.50	Case II 15,001,774.36
8%	Case I 12,695,643.57	Case III 13,004,043.23	Case IV 13,710,439.64	Case II 15,033,588.63
10%	Case I 12,592,214.51	Case III 13,129,490.12	Case IV 14,027,896.20	Case II 14,974,084.52

Figure 105: Influence of the evolution of the discount rate

Discount rate is the factor used to discount future cash flows in order to determine the net present value. An increasing discount rate is favorable for the models with high operational costs. This explains the moving forward of Case I and the regression of Case IV.

The discount rate to be used for such a project is not so easy to determine and should be obtained by analyzing similar, maritime, investments.

The cost and benefits analysis of some major harbor projects in Flanders and the Netherlands, such as Maasvlakte 2, uses 4% discount rate (Notteboom, 2011).

Christopher Bruce, Professor of Economics at the University of Calgary, estimates the future discount rate in Alberta (Canada) at 4.25% (Economica, 2007).

A study made by Grastos & Zachariadis, Life Cycle Cost of maintaining the effectiveness of a ships structure and environmental impact of ships design in 2010 uses discount rates of 5, 10 and 15%.

The report of the working group for shipbuilding and ship repair industry in India for the 11th 5 year plan 2007-2012 applies a discount rate of 11% and finally in the financial statements, dated 31/12/2010, of the Abu Dhabi ship building PJSC group 8 % is mentioned.

The discount rate used in this study is realistic but maybe a little on the low side.

The use of high tech paints and CRS (\approx low operational costs) is discouraged by a higher discount rate.

Influence of the inflation rate

Inflation rate 4, 6, 8 and 10% with a constant discount rate of 4%

Inflation rate	Cash Flow – discount rate 4 %			
4%	Case III 12,736,879.50	Case I 12,753,456.87	Case IV 13,174,993.50	Case II 15,001,774.36
6%	Case III 12,210,952.94	Case IV 12,270,036.84	Case I 12,693,737.73	Case II 14,774,510.90
8%	Case IV 10,807,263.65	Case III 11,265,967.82	Case I 12,394,721.11	Case II 14,189,826.32
10%	Case IV 8,474,503.25	Case III 9,639,312.57	Case I 11,660,361.12	Case II 12,987,670.80

Figure 106: Influence of the evolution of the inflation rate

Inflation is a rise in the general level of prices of goods and services in an economy. When the inflation rises the cost and the revenues far away in the future are most affected. In this case the scrap value of the ship, an income at the end of her economic life. Since the resell value of all the ships is nearly identical the model with the smallest operational cost benefits and this explains why Case IV becomes more beneficial when the discount rate increases.

As an example figure 107 illustrates the evolution of the inflation rate in China, the country of construction of our reference model.

The figure shows that the 6% inflation rate we used is most probably an under-estimation and that the inflation rate is rising and will keep on rising. This situation favors the construction in CRS.



Figure 107: China consumer price inflation (IMF, 2011)

10.9 Overall conclusion

Based on the reference model and supported by the sensitivity analysis the increased scantling technique, as applied in Case II can be classified as not economically healthy. The other construction methods are matched and the correct choice will be dependent on a lot of parameters, the most important being the steel price and the coating cost.

Since the basic commodities are getting scarcer the steel price will keep on rising. The CRS obtains its qualities by adding, amongst others, chromium and molybdenum, also 2 elements increasingly scarce. These arguments are favoring the use of improved coating systems. However, the coating cost is very sensitive. A little change in the cost of TSCF₂₅ is capable of reversing the economical ranking of the hypothetical cases.

Looking at the impact of the financial parameters and the ranking of the cases it seems that Case II is insensitive and most probably, in the future, Case III will be losing ground relative to Case IV. When it comes to Case I discount- and inflation rate seem to counterbalance each other.

11. Ballast free ships

11 Ballast free ships

11.1 Introduction

Ballast water and ballast water tanks are the source of a surging stream of problems.

In 1990, when the double hull construction was imposed from one day to the next, no consideration was given to the fact that corrosion would boost. Additionally, the corrosion problem was compounded by the ever growing issue of the migration of alien species.

On the other hand, the USA refuses any alternative, barring many solutions that might have been proposed by changing the existing legislation.

11.2 Ballast free ships

As the double hull construction is likely to remain a problem for the years to come, scientists started to look for possible alternative solutions. One very attractive and logical idea is the development of a ship without ballast.

However, all initiatives are still in an experimental stage: at this very moment not a single ship without ballast is sailing the world oceans.

11.3 Hull design solution

The ballast water free ships can be sub-divided into two categories, hull design solutions (11.3) and the flow through principle (11.4). The first group are the concepts where ballast becomes unnecessary thanks to an ingenious hull design.

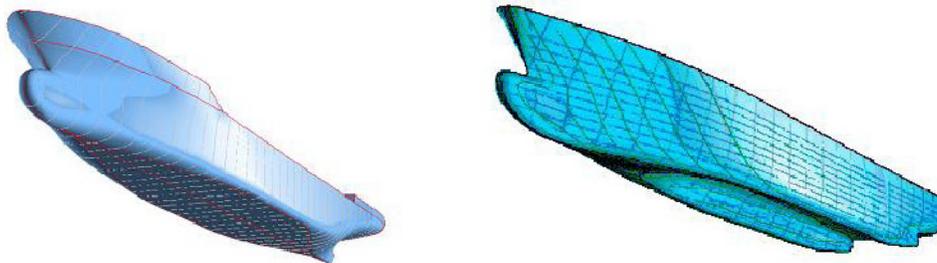


Figure 108: Conventional design versus ballast free ship (Aalbers, 2008)

Starting point is a mono-hull design with a bulbous bow. A recess in the bottom is provided starting from behind the bow till all the way aft. Purpose of this recess is to increase the draft when the ship is empty while loaded the draft should remain approximately the same as a conventional design.

The main disadvantage is that the wet surface and, hence, the sailing resistance both increase. This might be solved by creating an air cushion beneath the vessel.

11.4 Flow through principle

The second category of ships uses the so-called flow-through principle. These ships are not literally ballast free: they have ballast water on board, however, it is constantly being refreshed. As such, this ballast free ship concept involves a new paradigm that approaches ballast operation as the reduction of buoyancy, rather than as an addition of weight.

The traditional ballast tanks were replaced by two trunks running from fore to aft on each side of the ship. The port and starboard trunks are connected by a plenum at the stem and a second one at the stern.

The natural pressure distribution that develops around a hull at speed produces a positive relative pressure at the bow and a negative pressure at the stern. This pressure differential is used to drive a slow flow through the trunks so that they always contain "local water."

This design has been developed at the University of Michigan (USA).

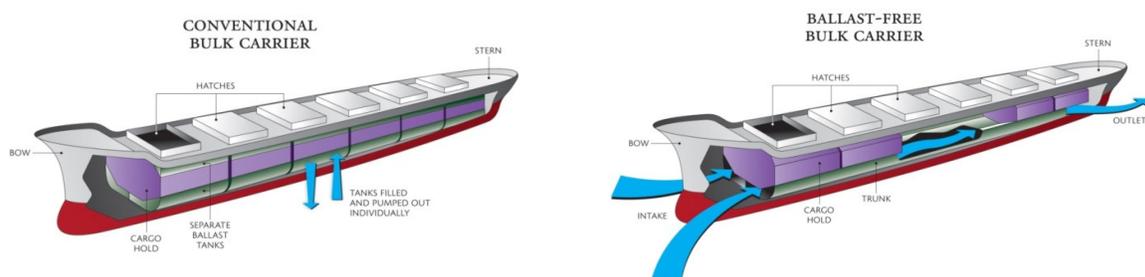


Figure 109: Difference between a conventional bulk carrier and a flow through bulk carrier (University of Michigan, 2010)

12. Conclusion and discussion

12 Conclusion and discussion

12.1 Introduction : “ is rust a must?”

The corrosion phenomenon came on board of ships together with the use of iron/steel elements. Steel was an appropriate alternative for wood becoming rare, and evidently the military aspect, with steel being more resistant to cannon balls than wood, is in this context not unimportant.

The transition from wood to iron did not happen overnight. The ship builders and designers needed time to get acquainted with this new material. Two developments are worthwhile mentioning, the first being the puddle process by Henry Cort allowing an industrial steel production of an improved quality, and secondly the introduction of welding techniques instead of riveting during World War II, making a fast production of ships possible.

Ballast on board of ships is a necessary evil. Ships without ballast cannot be steered or propelled. Till mid 19th century the ballast was dry and inert. Most of the time rocks were taken on board or thrown overboard in function of the necessity. When it became possible to construct ships completely out of metal, one could provide tanks that could be easily filled up with the most logical ballast material available, sea water.

Soon it became evident that every medal has two sides. The bright side shows the easy and fast handling of ballast in contrast with the dark side that represents the creation of corrosion friendly environments.

Till the end of the 20th century corrosion on board of ships had manageable dimensions. If you tackled this problem efficiently by a good maintenance strategy it was a fight that could be won.

Then, on a dark night in 1989, the Exxon Valdez struck the rocky shores of Prince William Sound in Alaska and caused an ecological disaster with a huge impact. Political motives gave birth to a hasty set of rules for the transport of oil in the territorial waters and EEZ of the USA: the Oil Pollution Act. This Act imposed the use of double hull tankers without providing alternatives. Ships who wanted to sail to the US had to be built according these rules. As the US is one of the superpowers in international trade, the rest of the world followed its demands. Concomitantly, all of sudden, the corrosion problem got out of control.

The double hull became the ideal location for all possible reinforcing elements of the hull structure. This narrow space of 2 meters width or height is crammed with complex metal constructions. It is self-evident that these spaces are used as ballast tanks. Ballast tanks are humid and hot, as a consequence of the thermos effect.

Due to the double hull construction the exposed surface rocketed and maintenance became hard or impossible because of bad accessibility. Ballast tanks are the Achilles heel of the double hull.

Corrosion is an electrochemical process during which the metal parts of the ship become anodic and literally resolve into the sea.

This discussion is about how to prevent this process from happening, how to slow it down and even how to stop it.

12.2 Research methodology

Many recent studies show corrosion algorithms and functions, given a generalized corrosion model. All these models are the result of prolonged laboratory studies. We intentionally selected another approach (see chapter 4). Taking advantage of our geographical position in the centre of the international port of Antwerp, we have surveyed a number of ships to assess the corrosion damage in situ. With the help of Antwerp Ship Repair, and many cooperative management companies and ship's crews, we were able to perform in situ inspections in the ballast tanks of 140 vessels, selected at random without interfering in their commercial activities.

The "in situ" aspect is a crucial element of this research program for a number of reasons. It puts us back in our natural environment. Ships are our habitat, not labs. In a lab it is feasible to determine the regression between corrosion rate and 1 or 2 parameters. The reality is much more complex because of multiple, often untraceable interactions between the circumstances.

12.3 Assessment of current solutions for the corrosion problem

12.3.1 Sacrificial anodes

As discussed in chapter 2 and 8, the sound electrochemical principle stipulates that by lowering the electrode-potential sufficiently the ship construction steel will become cathodic and the corrosion process will stop. However, our in situ observations indicate that sacrificial anodes on board of ships are inefficient. In brief - anodes do work, but not in ballast tanks.

Calculating the theoretical total mass of anodes required in a tank to obtain adequate protection is not so difficult. The new building specification for anodes in a coated tank is a mean current of 5mA/m^2 and a five year life expectancy for 50% ballast ratio. The average capacity of a Zn sacrificial anode is 780Ah/kg (see chapter 8). Approximately $0.16\text{ kg Zn per m}^2$ is required to obtain a standard protection.

However, when it comes to their effects in ballast tanks, anodes are at best working only half of the time, when the ballast tank is full. The immersion in an electrolyte is a condition sine qua non. It even takes a few days for an anode to deliver the necessary protective current. In the literature this figure varies between 1 and 4 days (Devanney, 2006). Consequently, on shorter ballast legs, anodes yield no effect.

Moreover, the operational range of an anode is limited by obstructions in the tank. This means that in every compartment a small anode should be provided instead of big anodes somewhere on an easy to reach spot.



Figure 110: A poorly sited anode (Amtec, 2008)

In addition, the quantity of anodes should evolve in time and in function of the condition of the coating. An intact coating requires very little cathodic protection while a coating in bad condition demands of a lot of sacrificial anodes.

To be effective, these anodes must be clean and free of deposit.

To summarize, if we choose to apply anodes it should be done the correct way or not at all.

The issue here for the regulators is whether or not to enforce proper cathodic protection. A way to impose a correct application and a follow up system is the provision of instructions and a control mechanism, similar to what is prescribed in the IMO performance standard for protective coatings (PSPC).

The usual practice for tankers is to periodically inspect the tank, look at the anodes, and guess how much zinc is left. However, the only way to check cathodic protection is to measure it. Fortunately, this is a simple process. All that is required is a reference voltage and a voltmeter. The reference voltage is provided by a half-cell. The half-cell is dropped into the tank and the potential between the half-cell and the steel is measured. If that voltage is high enough, we can be sure that there will be no immersed corrosion in the tank, even where the coating is defective. This day to day control could be done by the ships' crew by measuring of the tank polarization each ballast voyage. If the tank polarization is not up to 800mV (against a Ag-AgCl half cell) in four days, more anodes should be added (Devanney, 2010). In addition, whether the anodes are working will be evident through the colour of the tank. No red or brown should be visible were the tank coating has broken down, but instead, a white calcium-based precipitate should be present, which occurs when the steel is acting as a cathode (Devanney, 2010).



Figure 111: Effective anodes (Amtec, 2008)

12.3.2 Tank coatings

The application of a coating is the most common and the most evident anti-corrosion measure. The substrate is shielded from the electrolyte by an isolating layer.

Application of a coating is a very effective way of protecting the ship's steel as long as the coating is intact. On average we observed that the coating system remains intact for approximately 4 years and that afterwards the metal degrades at approximately 1.7% (surface) per year (see chapters 4 and 5 of this text).

The above mentioned values are the result of a statistical regression between the observed CI and the age of the ship. When visiting the tanks sometimes large differences could be observed between tanks of approximately the same age using the same coating system.

Three elements do certainly contribute to the coating performance standard.

Firstly, the design of the tank should be simple, avoiding places hard to reach and difficult to paint. The tank should drain sufficiently in order to avoid stagnating pools of ballast water when emptying.

Secondly, there is the paint itself. Only an approved paint system should be applied. Generally, modified epoxies are most commonly specified by

Chinese and Japanese builders, whereas Korean builders usually specify pure epoxy systems. Some 90 – 95% of WB tank spaces are now coated with either modified epoxy or pure epoxy systems, and probably less than 5% of these with solvent free epoxy systems. Solvent free epoxies will become more popular due to more stringent environmental regulations and health and safety issues in the ship building industry. Coal tar epoxy has been banned for some years now mainly because of health consequences. IMO PSPC also requires a light coloured coating to ease inspections (Towers, 2009). Most probably this will remain the case for the next few years. Alternative paint systems are surfacing. The use of polyurethanes seems to offer the best perspectives. A big advantage of these urethane based paints is that curing time is short and predictable allowing a shorter painting cycle during the construction (Safinah, 2009).

Lastly, there is the preparation of the surface, without any doubt the most critical element of the three. The successful performance of a ballast tank coating in service depends not only on the correct choice of the coating but also and mainly on the procedures adopted for surface preparation and paint application. Critical elements are amongst others; surface roughness, rounding of edges, removal of grease and salts, removal of dust, stripe coatings, dry film thickness, temperature and humidity control and a correct interval between the consecutive coatings.

8 December 2006, IMO adopted amendments to SOLAS by resolution MSC. 216(82) which mandate compliance with the new IMO "Performance Standard for Protective Coatings for dedicated seawater ballast tanks in all types of ships and double-side skin spaces of bulk carriers". IMO PSPC aims for a 15 year target life, with the coating remaining in GOOD condition. This is insufficient as the economical lifetime of a ship is 25 years. PSPC leaves the ship with inadequate protection during at least 40% of her lifetime.

Once the vessel is in service, coating repair and tank maintenance becomes difficult. Four options for tank coating management exist. Regular repairs can be done during normal dry docks, an upkeep by the crew on board is possible or a riding crew can be hired for extensive maintenance and the final option is a complete refurbishing of the ballast tank coating when catastrophic breakdown starts.

Combinations of the first three options are often chosen, but are very rarely successful in the long term. Most crew repairs last for a few months and then disbond from the steel and the old paint. Surface preparation with on board material is often difficult and the atmosphere in the ballast

tank is rarely suitable for paint application. More than once we noted during our observations that the ballast tanks were touched up with the wrong paint and in awful conditions.

Touch up repairs can be problematic and a poor long-term strategy, leaving the complete recoating of the tank as only reasonable solution (Lomas, 2008).

On the other hand, maintaining the coating in condition by paint repair jobs during dry docks or complete recoating jobs are expensive. The prices rocket due to extreme working condition, staging, ventilation, removal of grit and temperature control.

Only one conclusion is possible. Ballast tanks must become maintenance free throughout their economical life. Technically this is already perfectly possible. It is just a matter of getting things right from the beginning.

The tanker structure cooperative forum presented in 2000 during the shipbuilders meeting in Tokyo the TSCF₂₅ coating system with a design life of 25 years. Comparing IMO PSPC₁₅ with TSCF₂₅ teaches us that the differences are not that big. A better surface preparation, improved paint application conditions, an extra top coat and an increased extra dry film thickness. If we combine TSCF₂₅ with a corrosion hostile design of the tank, it must certainly be possible to come to solutions lasting the lifetime of the ship.

12.4 Dealing with the basics of corrosion: strategies for the future

Going back to the basics we know that for corrosion to occur in a neutral environment, 3 elements, oxygen, metal and an electrolyte are necessary. If one or more of these elements are not present, the corrosion will stop. This line of thinking is completely similar to fighting of fire and the fire triangle. For each element possible solutions can be formulated.



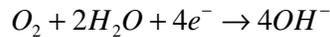
Figure 112: The corrosion triangle (own work)

12.4.1 Oxygen

The rate of corrosion depends on the oxygen concentration, partial pressure and temperature. The typical amount of dissolved oxygen in seawater is 9,6ppm (temperature dependent) (Smalwood, 2003).

Oxygen is a key element of the corrosion process in a ballast tank.

In a corrosion cell, at the cathode, the surplus of electrons causes the following reduction reaction.



The presence of dissolved oxygen in the water accelerates the cathodic reaction. The quantity of dissolved oxygen is function of the temperature, pressure and the salinity of the sea water (see figure 53, 2.6.1).

As shown by figure 52 (2.6.1), the corrosion rate increases in proportion to the amount of oxygen available for diffusion to the cathode.

At this moment techniques using inert gas are available to reduce the oxygen concentration in the ballast tanks when empty as well as when ballasted.

Inert gas on board of tankers is a gas containing less than 5% (vol) oxygen. Crude oil tankers use flue gas, being the treated exhaust gases of main engine or boiler. Product- and chemical tankers use inert gas generators producing inert gas by controlled combustion of diesel- or gas oil.

When ballast tanks are empty the oxygen rich atmosphere is replaced with inert gas by dilution or displacement. This process is called inerting and is standard practice for oil cargo tanks in order to reduce the explosion danger. The same inert gas in combination with a Venturi oxygen stripping system is used -to remove dissolved oxygen from the ballast water as it is drawn into the vessel. When taking the ballast water on board this water passes through the venture injector. A cavitation process shears the gas into a micro-fine emulsion in the water. The ballast water is now exposed to a gas containing much less oxygen than the air. As a new equilibrium is created, the oxygen diffuses from the liquid phase into the gas phase and at the same time small quantities of CO₂ and N₂ pass from the inert gas to the ballast water.

Initially, this inert gas contained too much sulphur. This was solved by adding a second water scrubber. The SO₂ concentration was lowered from >50 ppm tot less than 3 ppm. The ongoing corrosion process in the tanks

was stopped and the existing rust was converted from Fe_3O_4 to Fe_3O_2 (black magnetite). A very interesting aspect is that the same system can be used as ballast water management system avoiding the unwanted transfer of alien species from one biotope to another. Negative aspects are that anaerobic corrosion processes are not dealt with and the complex shape of the tank makes the inerting- and gas freeing process difficult.

12.4.2 Metal

To eliminate metal, different aspects have to be considered. The most radical solution is to abandon the use of metals completely and to start using only corrosion-free materials. Without any doubt very promising routes are to be discovered and most probably the construction of large size synthetic tanks will be made possible in the future. At this very moment however, we have to admit that no real alternatives are at hand.

A little bit less radical but actually more realistic is the use of corrosion resistant steel alloys (as discussed in chapter 10). The basic principle is that initially these alloys will corrode as fast as ordinary steel grades but after a while the layer oxides and hydroxides at the surface becomes so dense that the substrate beneath is shielded from the oxygen in the environment and corrosion is stopped. These steel grades are called "weathering" and a classical example is CorTen Steel. The density of the passivation layer is increased by adding copper and chrome to the alloy. Using these steel grades to construct ballast tanks is not advisable because the chlorides in the seawater destroy the protective layer and reactivate the corrosion process.

New and promising developments are imminent. Some important steel mills are experimenting with new combinations making the passivation protective film chloride proof. Chapter 10 shows that this inventive process is restrained by the maximum allowable price for corrosion resistant steel being 1.2 times the price of ordinary grade A steel (see figure 102).

12.4.3 Electrolyte

In a ballast tank, fresh or salt water acts as an electrical conductor. Fresh water is exceptionally used as ballast when the ship is discharging on a river or lake. Fresh water has a bad electric conductivity. The rate of corrosion is function of the diffusion of oxygen to the metal surface. The diffusion process increases at increased concentration of oxygen, temperature and speed (see figure 48). High concentrations of calcium and magnesium reduce the corrosion rate due to the formation of

carbonates lessening the spreading of oxygen to the metal surface (Exprosoft, 2009).

In salt water the rate of corrosion is higher due to the increased electric conductivity of the electrolyte. The presence of a large amount of NaCl, make it an excellent conductor. The chloride ions are particularly aggressive as they cause a breakdown of passivity causing pitting, crevice corrosion and stress corrosion cracking.

The chloride ion is also particularly aggressive as most chloride compounds are highly soluble, which limits the formation of polarizing anodic films (NAVFAC, 1992).

The concentration of NaCl in ocean water varies between 3 and 5%. The highest concentrations are met in the Mediterranean and the lowest in the Baltic Sea region (University of Waikato, 2010).

Figure 56 (2.6.1) shows that the corrosion rate increases in function of the salinity till a concentration of 3.5%. At higher NaCl concentrations the corrosivity diminishes due to the presence of less oxygen.

In chapter 7, Impact of tank construction parameters on the corrosion in ballast tanks on board of merchant vessels, we concluded that there was no statistical evidence of an influence of the navigational area on the corrosion rate.

Galvanic corrosion is impossible without an electrolyte. Two possibilities are open for discussion.

Treat the electrolyte, reduce the conductivity, use distilled water and remove the resolved oxygen. One possible line of thinking could be the re-using of ballast water. Treated ballast water would be transferred from special storage tanks ashore to the ships ballast tanks while discharging. When the ship is loaded the ballast water is not pumped over board but siphoned over to dedicated shore tanks.

An alternative is stop using ballast water completely and use dry inert ballast or develop ships where ballast is not needed anymore.

A traditional ship in unloaded transit needs ballast water to obtain full propeller immersion and sufficient forward draft to avoid bottom slamming. However, a lot of research has been done and we are on the eve of the construction of the first real ballast free ship. Two lines of reasoning have been followed (see chapter 11). The Michigan concept is based on a flow true system. The ballast is not permanent and considered

as a reduction of buoyancy rather than an addition of weight. The Dutch concept provides the necessary draft by an ingenious hull design and abandons the weight stability in favour of the form stability.

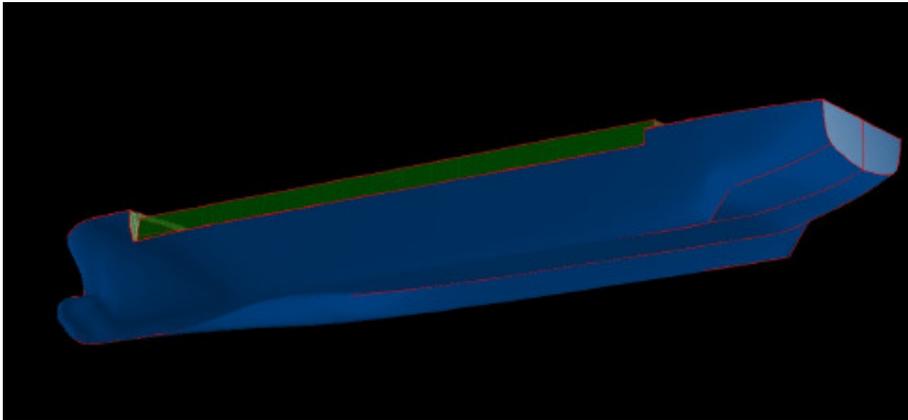


Figure 113: Ballast free ship (twin screw) – Dutch concept (Aalbers, 2008)

Ballast free ships also create an important ecological advantage. A VLCC in unloaded transit will normally carry between 80,000 and 100,000 tons of sea water containing countless organisms, potential harmful when released into foreign ecosystems without natural enemies. It has been estimated that in the 1990s ballast water may transport over 3,000 species of animals and plants a day around the world (NRC, 1995).

As an aside - after testing 140 ships we did not find any clear evidence of the occurrence of bacteriological contamination. None of the tanks visited showed any visual or other evidence of microbiologically induced corrosion. Discussions with experienced class surveyors corroborated our findings and made it clear that microbial induced corrosion in ballast tanks is, indeed, exceptional.

In summary, eliminating ballast on board creates a lot of advantages ranging from a serious reduction in fuel consumption on the ballast voyages to the creation of a maintenance friendly ship by clearing away the corrosion problem in ballast tanks.

12.5 Epilogue

Corrosion in ballast tanks is, as described in chapter 1, a problem rooted in the history of shipbuilding and in the physical need for ballast. If neglected it will endanger the safety of crew and ship, wreak economic havoc and possibly even cause damage to the environment.

It was the aim of this doctoral dissertation to tackle the problem of ballast tank corrosion, but from a unique perspective. Instead of following the reductionist approach by setting up lab experiments, designed to simulate the ballast tank environment, a more “ecological” approach was investigated, meaning that corrosion was studied in situ, in ballast tanks in a real life shipping situation. As such, we had to develop an instrument to adequately and concisely describe and determine corrosion progression in the tanks. The instrument to describe corrosion (as well as the possibly correlated environmental factors which influence the corrosion process) has been developed at the beginning of the project in the shape of a questionnaire and a photo taking methodology (chapter 4 and annex IV); determination of the corrosion level occurred using the CI developed in chapter 5. Both instruments (as well as the methodological insights linked with them) can be used in further in situ analysis work.

Application of these instruments and methodology to a set of over 140 actual merchant ships has offered us the possibility to test them in a real life situation. Firstly, a number of general parameters were tested to reveal if they impacted corrosion progression in ballast tanks (chapter 7). To do so in a convincing manner, a statistical model (based on a logistic transformation) as well as a way to perform an ANOVA on this kind of data had to be added to the instrumentarium.

The proof of the pudding lies, as always, in the eating. Using the complete instrumentarium, the question could be addressed whether sacrificial anodes contribute significantly to an extension of the operational life of a tank. Contrary to the widely spread insight that sacrificial anodes, possibly combined with a coating, are functional in lab-based models and in many real-life situations (such as oil drill platforms and other continuously submerged iron constructions), the data presented in this manuscript (chapter 9) indicate that this insight is difficult to apply to the ballast tank environment, probably due to its complex geometry and to the absence of validated guidelines on how to install these anodes effectively. This unequivocal result further supports the choice made for this research project, namely, to work from an in situ point of view. As such projects will probably become even more important in the near future; it is our

hope that the methodological basis laid in chapters 4, 5 and 7 of this thesis will be of good use to other in situ researchers.

Finally, this dissertation wanted to offer options to avoid ballast tank corrosion. Two solutions are possible. Either we design a ship without ballast tanks, or we combine different engineering ideas in order to create a corrosion resistant ballast tank concept. The latter approach was taken for a first level economic analysis (chapter 10). This analysis demonstrated that both the substitution of the present coating with a more durable variety, and the construction of ships using corrosion-resistant steel types are economically viable within what can reasonably be expected in the coming decennia. Either way, a radical rethinking of the concept of ballast is needed to free the future generations of ships of the corrosion problem.

The economic analysis brings us also immediately to two key research lines into perspective for the near future. First, there is the option to design and compare different coating types, in terms of their physicochemical resistance against the duress to be expected in a ballast tank environment, as well as in terms of their ecotoxicological inertia. Secondly, one should take up the design of corrosion-resistant steel types. As in situ analysis of innovative steel or coating types would be rather impossible (as there are no ships sporting either innovative material), a new technical challenge will therefore lie in the set-up of a test system. Further on, characteristics of coatings and steel types can be correlated with possible corrosion progression (or the absence thereof) of the samples, leading to innovative engineering solutions for an age-old problem.

For indeed, "rust is not a must."

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16 Abbreviations

%PD	Percent paint damage
A	Frequency factor
a	Number of anodes
ANOVA	Analysis of variance
AS	Purchase price grade A steel in €/ton
ASA	Useful surface area of the anode
B	Proportionality constant
b	Slope of the Tafel line
BOD	Biological oxygen demand
C	Concentration
C1	Factor quantifying the fraction of ASR/LWT caused exclusively by corrosion in function of the time
CA	Corrosion allowance in mm
CAN	Cost new building in grade A steel quality in €/ton
CCRS	Cost coating /re-coating CRS in €
CDD	Cost rental dry dock in €/day
CE	Local breakdown of coating or rust on edge or weld lines
CI	Corrosion index
CNRS	Cost new building in CRS quality in €/ton
C _o	Concentration in the bulk solution
COD	Chemical oxygen demand
CP	Breakdown of coating or area rusted on plates
CRS	Corrosion Resistant Steel
CRS	Purchase price CRS in €/ton
Cs	Specific heat [J/(K·kg)]

D	Diffusion coefficient	
DC	Direct current	
DENS	Steel Density	[t/m ³]
DFT	Dry Film Thickness	
DWT:	Deadweight in ton	
E	Driving potential	
E	Internal energy	[Joule, J]
E	Reduction potential	[Volt, V]
E_{298}^0	Standard reduction potential (25°C & 1bar)	
E_a	Activation energy	[Joule, J]
E_{corr}	Corrosion potential	[Volt, V]
E_{eq}	Equilibrium potential	[Volt, V]
E_k	Kinetic energy	[Joule, J]
EMF	Electromotive Force	[Volt, V]
E_p	Passivation potential	[Volt, V]
E_r	Reversible potential	[Volt, V]
E_t	Transpassive potential	[Volt, V]
F	Faraday's constant	[C/Mol]
G	Gibbs energy (Free energy)	[Joule, J]
G_{298}^0	Free energy (25°C & 1bar)	[Joule, J]
H	Enthalpy	[Joule, J]
H_{298}^0	Enthalpy (25°C & 1bar)	[Joule, J]
I	current density	
i	Current density	[A/m ²]
I	Current	[Ampere, A]
i_0	Exchange current density	[A/m ²]

I_0	Exchange current	[Ampere, A]
IA	Installation cost anodes in €/piece	
i_a	Anodic current density	[A/m ²]
I_a	Anodic current	[Ampere, A]
IACS	International Association of Classification Societies	
I_{anode}	Delivered current per sacrificial anode	
I_c	Cathodic current	[Ampere, A]
i_c	Cathodic current density	[A/m ²]
I_{corr}	Corrosion current	[Ampere, A]
i_{corr}	corrosion current density	[A/m ²]
i_{cp}	Current density at critical passivation	
i_g	Layer current density	[A/m ²]
I_g	Layer current	[Ampere, A]
i_p	Current density at passivation	[A/m ²]
IRB	Iron reducing bacteria	
I_{required}	Required counter current for cathodic protection	
i_{required}	Required current density	
k	Boltzmann constant	
K	Equilibrium constant	
LPR	Linear Polarization Resistance	
LWT	Lightweight in ton	
LWT_T	Light weight tank type I, III and IV in ton	
LWT_{TII}	Lightweight tank type II in ton	
m	Meter	
M	Molar mass	[gmol ⁻¹]
m, n.....	Number of atoms, mol, electrons	

MCA	Maritime and Coastguard Agency	
mm	Millimetre	
N	Number of anodes	
OPP	Surface ballast tanks in m ²	
ORP	Oxidation/reduction potential	
P	Pressure	[Pascal, Pa]
pH	Measure of acidity	
PSPC	Performance Standard for Protective Coatings	
PSPC ₁₅ expectancy	Coating according PSPC standards – 15 years lifetime	
q	Electrical charge	[Coulomb, C]
q	Heat	[Joule, J]
Q	Reaction quotient	
q _{rev}	Heat released or absorbed In a reversible process	
R	Ideal gas constant	[JK ⁻¹ mol ⁻¹]
RA	Replacement of anodes in €/piece	
RAS	Replacement of steel in €/ton	
R _p	polarization resistance	[Ohm, Ω]
RPSPC	Cost of repairing PSPC ₁₅ in €/m ²	
RTSCF	Cost of repairing TSCF ₂₅ in €/m ²	
S	Entropy	[Joule/Kelvin]
SA _{total}	Total surface area to be protected	
SCE	Saturated Calomel Electrode	
SCI	Scrap per ton grade A steel in €/ton	
SHE	Standard Hydrogen Electrode	
SRB	Sulphur-reducing bacteria	

sur	Surroundings	
sys	System	
T	Temperature	[Kelvin, K]
t	Time	[Second, s]
TC	Time charter equivalent in €/day	
TSCF	Tanker Structure Cooperative Forum	
TSCF ₂₅ expectancy	Coating according TSCF standards – 25 years lifetime	
U	Internal energy	[Joule, J]
u	Specific internal energy	[Jmol ⁻¹]
ULCC	ultraUltra-large crude carrier	
univ	Universe	
v	Speed	[m/s]
V	Volume	[m ³]
VSS%	volatile suspended solids	
W	Number of microstates	
w	Work	[Joule, J]
WFT	Wet Film Thickness	
α	Transfer coefficient	
δ	layer thickness	[meter]
η	Overpotential (E-E _{eq})	[Volt, V]

17 Annex I: Construction steel, Lloyds Register of Shipping, 2006

Table 2.2.1 Material classes

Structural member	Material class		
	Within 0,4L amidships	Between 0,4L and 0,6L amidships	Outside 0,6L amidships
Where $L > 250$ m: Sheerstrake or rounded gunwale Stringer plate at strength deck	V	III	II
Where $L \leq 250$ m: Sheerstrake or rounded gunwale Stringer plate at strength deck	IV	III	II
Bilge strake (see Note 4) Deck strake in way of longitudinal bulkhead			
Strength deck plating (see Note 5) Bottom plating including keel Continuous longitudinal members above strength deck Upper strake of longitudinal bulkhead Upper strake of topside tank	III	I	I
Deck plating, other than above, exposed to weather Side plating Lower strake of longitudinal bulkhead	II	I	I
External plating of rudder horn	—	—	III
Sternframe Internal components of rudder horn Rudder Shaft bracket	—	—	II

NOTES to Tables 2.2.1 and 2.2.2

- For structural members not listed, Class I may generally be applied.
- Within 0,4L amidships, single strakes required to be of Class IV, Class V or of Grade E are to have breadths not less than $800 + 5L$ mm but need not be greater than 1800 mm.
- In ships with breadth exceeding 70 m at least five deck strakes including stringer plates are to be of Class IV within 0,4L amidships.
- Bilge strakes may be of Class III within 0,4L amidships in ships with a double bottom over the full breadth and with length less than 150 m.
- For the requirements for material class of plating of main cargo hatchway openings see:
 - Pt 3, Ch 5,2.5 – Fore end structure
 - Pt 3, Ch 6,2.5 – Aft end structure
 - Pt 4, Ch 1,4.5 – General cargo ships
 - Pt 4, Ch 7,4.3 – Bulk carriers
 - Pt 4, Ch 8,4.6 – Container ships
 - Pt 4, Ch 11,4.2 – Ore carriers
- The material class used for reinforcement and the quality of material (i.e. whether mild or higher tensile steel) used for welded attachments, such as waterway bars and bilge keels, is to be similar to that of the hull envelope plating in way. Where attachments are made to rounded gunwale plates, special consideration will be given to the required grade of steel, taking account of the intended structural arrangements and attachment details.
- The material class for deck plating, sheerstrake and upper strake of longitudinal bulkhead within 0,4L amidships is to be maintained at the poop front and at ends of the bridge where fitted.
- For container ships, the strength deck, sheerstrake and torsion box structure material classes within 0,4L amidships are to be maintained in way of the cargo hold region.
- On tankers having a poop, the quality of strength deck plating in way of the poop front is to be extended forward to cover any pump room openings.
- Engine seat top plates outside 0,6L amidships of thickness greater than 40 mm, may be Grade A mild steel. Steel grade requirement for top plates within 0,6L amidships will be specially considered.
- Steel grade is to correspond to the as fitted thickness when this is greater than the Rule requirement.

Table 2.2.2 Steel grades

Thickness, <i>t</i> in mm	Class									
	I		II		III		IV		V	
	Mild steel	H.T. steel								
$t \leq 15$	A	AH	A	AH	A	AH	A	AH	D	DH
$15 < t \leq 20$	A	AH	A	AH	A	AH	B	AH	E	DH
$20 < t \leq 25$	A	AH	A	AH	B	AH	B	AH	E	DH
$25 < t \leq 30$	A	AH	A	AH	D	DH	E	DH	E	DH
$30 < t \leq 35$	A	AH	B	AH	D	DH	E	DH	E	DH
$35 < t \leq 40$	A	AH	B	AH	D	DH	E	DH	E	DH
$40 < t \leq 50$	B	AH	D	DH	E	DH	E	DH	E	DH
$t > 50$	B	AH	D	DH	E	DH	E	DH	E	DH

See Notes under Table 2.2.1

Table 2.2.3 Grades of steel for minimum design temperatures below 0°C

Minimum design temperature, in °C	Thickness, in mm	Grades of steel
0 to -10	$t \leq 12,5$	B/AH
	$12,5 < t \leq 25,5$	D/DH
	$t > 25,5$	E/EH
-10 to -25	$t \leq 12,5$	D/DH
	$t > 12,5$	E/EH
-25 to -40	$t \leq 12,5$	E/EH
	$t > 12,5$	C-Mn LT 60 or 1/2 Ni steels (see also Pt 2, Ch 3,6)

Table 2.2.4 Assessment of deck temperature

Arrangement	Deck temperature
(1) Deck not covered with insulation in the refrigerated space	Temperature of the refrigerated space
(2) Deck covered with insulation in the refrigerated space and not insulated on the other side	Temperature of the space on the uninsulated side
(3) Deck covered with insulation on both sides	Mean of the temperatures of the spaces above and below the deck less 3°C
(a) Temperature difference not greater than 11°C	
(b) Temperature difference greater than 11°C but not greater than 33°C	
(c) Temperature difference greater than 33°C	Deck temperature will be specially assessed
NOTE Where one of the internal spaces concerned is not refrigerated, the temperature of the space is to be taken as 5°C.	

2.3 Grades of steel for ice-breaking ships designed to operate in low ambient temperatures

2.3.1 These requirements are intended for ships strengthened in accordance with the Requirements stated in Ch 9,8 and Ch 9,9 and designed to operate for long periods in low air temperatures.

2.3.2 The grade of steel to be used is related to the anticipated operating temperature, T_0 , degree of ice induced dynamic loading and the thickness of material. In no case should the grade of steel be less than that required by 2.1 or 2.2.

2.3.3 In order to establish the anticipated operating temperature, T_0 , for a given structural member it is assumed that the minimum design air temperature, T , for ships designed to operate in Arctic or Antarctic conditions, is not lower than -45°C and should not be taken as higher than -35°C. It is the responsibility of the Owner to specify the design air temperature T . Where reliable environment records for contemplated operational areas exist, the minimum design air temperature can be obtained after the exclusion of all recorded values having a probability of occurrence of less than 3 per cent. If T is lower than -45°C then the steel grades to be used will be specially considered.

2.3.4 The operating T_0 relevant for the selection of steel grades is given in Table 2.2.5.

2.3.5 Steel grades for plating forming the outer shell and deck boundaries are obtained from the figures specified in Table 2.2.5. The strakes of shell plating to which the bilge keels or ground bars are attached are to be made of Grade D steel over the forward 0,5L but may be of Grade B steel elsewhere.

2.3.6 In general, longitudinal frames and longitudinal bulkhead strakes attached to deck and shell and outboard strakes of horizontal stringers are to be of the same steel grade as the hull envelope plating to which they are connected, but the grade may be adjusted to take account of difference in thickness.

2.3.7 The outer strake of web plating of web frames is to be constructed of material of the same steel grade as the shell plating to which they are attached, but the grade may be adjusted to take account of difference in thickness.

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Designation: A 131/A 131M - 89

Standard Specification for Structural Steel for Ships¹

This standard is issued under the fixed designation A 131/A 131M; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reappraisal. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reappraisal.

1. Scope

1.1 This specification covers structural steel shapes, plates, bars, and rivets intended primarily for use in ship construction.

1.2 Material under this specification is available in the following categories:

Ordinary Strength—Grades A, B, D, DS, CS, and E with a specified minimum yield point of 34 ksi [235 MPa], and

Higher Strength—Grades AH, DH, and EH with specified minimum yield points of either 46 ksi [315 MPa] or 51 ksi [350 MPa].

1.3 Shapes and bars are normally available as Grades A, AH32, or AH36. Other grades may be furnished by agreement between the purchaser and the manufacturer.

1.4 When the steel is to be welded, it is presupposed that a welding procedure suitable for the grade of steel and intended use or service will be utilized.

1.5 The values stated in either inch-pound units or SI units are to be regarded separately as the standard. Within the text, the SI units are shown in brackets. The values stated in each system are not exact equivalents; therefore, each system must be used independently of the other. Combining values from the two systems may result in nonconformance with this specification.

2. Referenced Documents

2.1 ASTM Standards:

A 6/A 6M Specification for General Requirements for Rolled Steel Plates, Shapes, Sheet Piling, and Bars for Structural Use²

A 370 Test Methods and Definitions for Mechanical Testing of Steel Products²

E 112 Test Methods for Determining the Average Grain Size³

3. General Requirements for Delivery

3.1 Material furnished under this specification shall conform to the applicable requirements of the current edition of Specification A 6/A 6M. These include the requirements for analysis, test preparation, method of test, permissible variations in dimensions and weight, quality, marking, inspection, retests, rejection, packaging and loading, etc., except as modified herein. Conditioning shall be in accordance with

Specification A 6/A 6M except that after removal of any imperfection preparatory to welding the thickness of the plate at any location must not be reduced by more than 20 % of the nominal thickness of the plate.

4. Ordering Information

4.1 Inquiries, orders, contracts, etc., for material to this specification should include the following information to describe adequately the desired material:

4.1.1 Quantity (weight or number of pieces),

4.1.2 Name of material (ordinary strength or higher strength; carbon steel shapes, plates, bars, or rivets),

4.1.3 ASTM specification designation, grade, and year of issue,

4.1.4 Cold flanging when applicable,

4.1.5 Dimensions,

4.1.6 Condition (hot rolled or hot rolled and normalized), and

4.1.7 Supplementary requirements, if any.

5. Manufacture

5.1 Melting Process:

5.1.1 The steel may be made by any of the following processes: open-hearth, basic-oxygen, electric-furnace, vacuum arc remelt (VAR), or electroslag remelt (ESR).

5.1.2 Except for Grade A steel up to and including ½ in. [12.5 mm] in thickness, rimming-type steels shall not be applied.

5.1.3 Grades AH32 and AH36 shapes through 426 lb/ft, and plates up to 0.5 in. [12.5 mm] in thickness may be semi-killed, in which case the 0.10 % minimum silicon does not apply.

5.1.4 Except as permitted in 5.1.4.1, Grades D, DS, CS, E, DH32, DH36, EH32, and EH36 shall be made using a fine grain practice. For ordinary strength grades, aluminum shall be used to obtain grain refinement. For high strength grades, aluminum, vanadium, or columbium (niobium) may be used for grain refinement.

5.1.4.1 Grade D material 1½ in. [35 mm] and under in thickness, at the option of the manufacturer, may be semi-killed and exempt from the fine austenitic grain size requirement of 8.1, but such material shall be subject to the toughness requirement of 9.2.1.

6. Heat Treatment

6.1 Plates in all thicknesses ordered to Grades CS and E shall be normalized. Plates over 1½ in. [35 mm] in thickness ordered to Grade D shall be normalized. When Grade D steel is furnished semi-killed, it shall be normalized over 1 in. [25 mm] in thickness. Upon agreement between the purchaser and the manufacturer, control rolling of Grade D steel may be substituted for normalizing, in which case impact

¹ This specification is under the jurisdiction of ASTM Committee A-1 on Steel, Stainless Steel, and Related Alloys and is the direct responsibility of Subcommittee A01.02 on Structural Steel for Bridges, Buildings, Rolling Stock, and Ships.

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² Annual Book of ASTM Standards, Vol 01.04.

³ Annual Book of ASTM Standards, Vol 03.01.

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tests are required for each 25 tons [25 Mg] of material in the heat.

6.2 Plates in all thicknesses ordered to Grades EH32 and EH36 shall be normalized. Grades AH32, AH36, DH32, and DH36 shall be normalized when so specified in Table 1. Upon agreement between the purchaser and the manufacturer, control rolling of Grade DH may be substituted for normalizing, in which case impact tests are required on each plate.

TABLE 1 Heat Treatment Requirements for Higher Strength Grades (32 and 36)^a

Aluminum-treated steels:	
AH32 or AH36	Normalizing not required up to and including 2 in. [50 mm] in thickness
DH32 or DH36	Normalizing required over 1.0 in. [25 mm]
EH32 or EH36 Normalized	
Columbium (niobium) or vanadium-treated steels:	
AH32 or AH36	Normalizing not required up to and including 2 in. [50 mm] in thickness
DH32 or DH36	Normalizing required over 0.50 in. [12.5 mm]
EH32 or EH36 Normalized	

^a When columbium (niobium) or vanadium is used in combination with aluminum, heat treatment requirements for columbium or vanadium apply.

6.3 In the case of shapes, the thicknesses referred to are those of the flange.

7. Chemical Requirements

7.1 The heat analysis shall conform to the requirements for chemical composition prescribed in Table 2.

7.1.1 The steel shall conform on product analysis to the requirements prescribed in Table 2, subject to the product analysis tolerances in Specification A 6/A 6M, except as specified in 7.1.2.

7.1.2 Product analysis is not required for bar-size shapes or flat bars ½ in. [12.5 mm] and under in thickness.

7.1.3 When tension tests are waived in accordance with 9.1.1.2, chemistry consistent with the mechanical properties desired must be applied.

8. Metallurgical Structure

8.1 Fine grain practice for ordinary strength grades shall be met using aluminum. For higher strength grades, aluminum, vanadium, or columbium may be used as grain refining elements.

8.2 Except as modified by 8.2.1, grain size shall be determined on each heat by the McQuaid-Ehn test of Methods E 112. The grain size so determined shall be No. 5 or finer in 70 % of the area examined.

8.2.1 As an alternative to the McQuaid-Ehn test, a fine grain practice requirement may be met by a minimum acid-soluble aluminum content of 0.015 % or minimum total aluminum content of 0.020 % for each heat.

8.2.2 For Grades DH32, DH36, EH32, and EH36 the fine grain practice requirement may also be met as follows:

8.2.2.1 Minimum columbium (niobium) content of 0.020 % or minimum vanadium content of 0.050 % for each heat, or

8.2.2.2 When vanadium and aluminum are used in combination, minimum vanadium content of 0.030 % and minimum acid-soluble aluminum content of 0.010 %, or minimum total aluminum content of 0.015 %.

9. Mechanical Requirements

9.1 Tension Tests:

9.1.1 Except as specified in the following paragraphs the material as represented by the test specimens shall conform to the tensile requirements prescribed in Table 3.

TABLE 2 Chemical Requirements

Element	Composition, %						
	Ordinary Strength Grades						Higher Strength Grades
	A	B	D	E	CS	DS	AH32, AH36, DH32, DH36, EH32, and EH36
Carbon, ^a max	0.23 [#]	0.21	0.21	0.18	0.16	0.16	0.18
Manganese ^a	0	0.80-1.10 ^o	0.70-1.35 ^{o,e}	0.70-1.35 ^o	1.00-1.35 ^o	1.00-1.35 ^o	0.90-1.60
Phosphorus, max	0.05	0.04	0.04	0.04	0.04	0.04	0.04
Sulfur, max	0.05	0.04	0.04	0.04	0.04	0.04	0.04
Silicon	...	0.35 max	0.10-0.35 ^f	0.10-0.35	0.10-0.35	0.10-0.35	0.10-0.50 ^g
Nickel, max	0.40 ^{g,h}
Chromium, max	0.25 ^{g,h}
Molybdenum, max	0.08 ^{g,h}
Copper, max	0.35 ^{g,h}
Columbium (niobium), max	0.05 ^{h,i}
Vanadium, max	0.10 ^{h,i}
Aluminum

^a For all ordinary strength grades, the carbon content plus ½ of the manganese content shall not exceed 0.40 %.

[#] A maximum carbon content of 0.26 % is acceptable for Grade A plates equal to or less than ½ in. [12.5 mm] and all thicknesses of Grade A shapes.

^o Grade A plates over ½ in. [12.5 mm] in thickness shall have a minimum manganese content not less than 2.5 times the carbon content. Grade A shapes and bars are not subject to the manganese/carbon ratio of 2.5.

^e For all ordinary strength grades, the upper limit of the manganese may be exceeded up to 1.65 % provided carbon content plus ½ of manganese content does not exceed 0.40 %. The lower limit of the manganese for Grade B may be reduced to 0.60 % when the silicon content is 0.10 % or more or when cold-flanging material is specified.

^f For Grade D steel equal to or less than 1.00 in. [25 mm] in thickness, 0.60 % minimum manganese content is acceptable.

^g Lower limit of silicon does not apply to semi-killed Grade D steel.

^h See 5.1.3.

ⁱ These elements need not be reported on the mill sheet unless intentionally added.

^j See Section 8.

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TABLE 3 Tensile Requirements

	Ordinary Strength Grades (A, B, D, DS, CS, and E)				Higher Strength Grades			
	Structural Steel		Rivet Steel and Steel for Cold Flanging		AH32, DH 32, and EH32		AH36, DH36, and EH36	
	ksi	[MPa]	ksi	[MPa]	ksi	[MPa]	ksi	[MPa]
Tensile strength	58 to 71 ^A	[400 to 490]	55 to 65	[380 to 450]	68 to 85	[470 to 585]	71 to 90	[490 to 620]
Yield point, min	34 ^B	[235 ^B]	30	[205]	46	[315]	51	[360]
Elongation in 8 in. [200 mm], min, %	21 ^{C,D,E}		23 ^C		19 ^C		19 ^C	
Elongation in 2 in. [50 mm], min, %	24 ^{D,E}		26		22		22	

^A A tensile strength range from 58 to 80 ksi [400 to 550 MPa] may be applied to Grade A shapes.
^B For Grade A over 1 in. [25 mm] in thickness, the minimum yield point may be reduced to 32 ksi [220 MPa].
^C For nominal thicknesses or diameters under 1/8 in. [8 mm], a deduction from the specified percentage of elongation in 8 in. [200 mm] shall be made for decreases of the nominal thickness or diameter below 1/8 in. [8 mm]. See elongation requirement adjustments under the Tension Tests section of Specification A 6/A 6M for deduction values.
^D For nominal thicknesses or diameters over 3.5 in. [90 mm], a deduction from the specified percentage of elongation in 2 in. [50 mm] shall be made for increases of the nominal thickness or diameter above 3.5 in. [90 mm]. See elongation requirement adjustments under the Tension Tests section of Specification A 6/A 6M for deduction values.
^E Elongation not required to be determined for floor plate.

9.1.1.1 Unless a specific orientation is called for on the purchase order, tension test specimens may be taken parallel or transverse to the final direction of rolling at the option of the steel manufacturer.

9.1.1.2 Shapes less than 1 in.² [645 mm²] in cross section, and bars, other than flats, less than 1/2 in. [12.5 mm] in thickness or diameter need not be subjected to tension tests by the manufacturer.

9.1.1.3 The elongation requirement of Table 3 does not apply to material ordered as floor plates with a raised pattern. However, for floor plates over 1/2 in. [12.5 mm] in thickness, test specimens shall be bent cold with the raised pattern on the inside of the specimen through an angle of 180° without cracking when subjected to a bend test in which the inside diameter is three times plate thickness. Sampling for bend testing shall be as specified for the tension tests in 9.1.2.

9.1.2 One tension test shall be made from each of two different plates, shapes, or bars from each heat of structural steel and steel for cold flanging unless the finished material from a heat is less than 50 tons [45 Mg], when one tension test will be sufficient. If, however, material from one heat differs 1/8 in. [10 mm] or more in thickness or diameter, one tension test shall be made from both the thickest and the thinnest material rolled, regardless of the weight represented.

9.1.3 Two tension tests shall be made from each heat of rivet steel.

TABLE 4 Charpy V-Notch Requirements for Maximum Thickness of 2 in. [50 mm]

Grade and Test Temperature	Longitudinal Specimens, min avg		Transverse Specimens, min avg	
	ft-lbf	[J]	ft-lbf	[J]
B ^A at 32°F [0°C]	20	[27]	14	[19]
D ^B at +14°F [-10°C]	20	[27]	14	[19]
E at -40°F [-40°C]	20	[27]	14	[19]
AH32 ^B at 32°F [0°C]	25	[34]	17	[23]
DH32 ^B at -4°F [-20°C]	25	[34]	17	[23]
EH32 at -40°F [-40°C]	25	[34]	17	[23]
AH36 ^B at 32°F [0°C]	25	[34]	17	[23]
DH36 ^B at -4°F [-20°C]	25	[34]	17	[23]
EH36 at -40°F [-40°C]	25	[34]	17	[23]

^A Impact tests are not required for Grade B 1 in. [25 mm] and under in thickness.
^B See 9.2.1.

9.2 **Toughness Tests** (material 2 in. [50 mm] and less in thickness):

9.2.1 Except as permitted in 9.2.1.1, Charpy V-notch tests shall be made on Grade B material over 1 in. [25 mm] in thickness and on material of Grades D, E, AH32, AH36, DH32, DH36, EH32, and EH36. The test results shall conform to the requirements of Table 4.

9.2.1.1 Toughness tests are not required: (a) on Grade D normalized material made fully killed and having a fine austenitic grain size, (b) on Grades AH32 and AH36 when normalized, or when 0.5 in. [12.5 mm] or less in thickness when treated with vanadium or columbium (niobium) or 1 1/8 in. [35 mm] or less in thickness when treated with aluminum, and (c) on Grades DH32 and DH36 material when normalized.

9.2.2 For plate material, when required, one set of three impact specimens shall be made from the thickest material in each 50 tons [45 Mg] of each heat of Grades B, D, AH32, AH36, DH32, and DH36 steels and from each rolled product of normalized Grades E, EH32, and EH36 steels. When heat testing is called for, a set of three specimens shall be tested for each 50 tons [45 Mg] of the same type of product produced on the same mill from each heat of steel. The set of impact specimens shall be taken from different as-rolled or heat-treated pieces of the heaviest gage produced. An as-rolled piece refers to the product rolled from a slab, billet, bloom, or directly from an ingot. For flats, rounds, and shapes, one set of three impact tests shall be taken from each 25 tons [25 Mg] of each heat for Grade E, EH32, or EH36 and, when required, from each 50 tons [45 Mg] of each heat of Grade B, D, AH32, AH36, DH32, or DH36 material. Where the maximum thickness or diameter of various sections differs by 1/8 in. [10 mm] or more, one set of impacts shall be made from both the thickest and the thinnest material rolled regardless of the weight represented.

9.2.3 The specimens for plates shall be taken from a corner of the material and the specimens from shapes shall be taken from the end of a shape at a point one third the distance from the outer edge of the flange or leg to the web or heel of the shape. Specimens for bars shall be in accordance with Specification A 6/A 6M.

9.2.4 The center longitudinal axis of the specimens shall be located as near as practical mid-way between the surface

and the center of the material and the length of the notch shall be perpendicular to the rolled surface.

9.2.5 Unless a specific orientation is called for on the purchase order, the longitudinal axis of the specimens may be parallel or transverse to the final direction of rolling of the material at the option of the steel manufacturer.

9.2.6 The impact test shall be made in accordance with the simple beam, Charpy V-notch type of test described in Sections S23 and S24 of Methods and Definitions A 370.

9.2.7 Each impact test shall constitute the average value of three specimens taken from a single test location. The average value shall meet the specified minimum with not more than one value below the specified minimum but in no case below two thirds of the specified minimum. If these requirements are not met, a retest of three additional specimens may be made as follows:

9.2.7.1 Retest three additional specimens, each of which must equal or exceed the minimum average energy value specified.

9.2.7.2 If the required energy values are not obtained upon retest, the material may at the option of the producer be heat treated in the case of as-rolled material or reheat treated in the case of heat-treated material.

9.2.7.3 After heat treatment or reheat treatment a set of three specimens shall be tested and evaluated in the same manner as for the original material.

9.2.7.4 If the impact test result fails to meet the requirement for the thickest product tested when heat testing, that material shall be rejected and the next thickest material may be tested to qualify the balance of the heat in accordance with 9.2.7. At the option of the producer retests may be made on each piece of the rejected material, in which case each piece shall stand on the results of its own test. It shall also be the option of the producer to heat treat the product prior to retesting if desired.

9.3 **Toughness Tests** (material over 2 in. [50 mm] thick):

9.3.1 Charpy V-notch tests are required for all grades of steel over 2 in. [50 mm] thick, except for Grade A that is produced killed, using a fine grain practice and normalized.

TABLE 5 Charpy V-Notch Requirements for Thicknesses Over 2 in. [50 mm]

Grade and Test Temperature	Longitudinal Specimens, min avg		Transverse Specimens, min avg	
	ft-lbf	[J]	ft-lbf	[J]
A ^a at +68°F [+20°C]	20	[27]	14	[19]
B at +32°F [0°C]	20	[27]	14	[19]
D at +14°F [-10°C]	20	[27]	14	[19]
DS at +14°F [-10°C]	20	[27]	14	[19]
CS at -40°F [-40°C]	20	[27]	14	[19]
E at -40°F [-40°C]	20	[27]	14	[19]
AH32 and AH36 at +32°F [0°C]	25	[34]	17	[23]
DH32 and DH36 at -4°F [-20°C]	25	[34]	17	[23]
EH32 and EH36 at -40°F [-40°C]	25	[34]	17	[23]

^a See 9.3.1.

9.3.2 For plate material one set of three impact specimens shall be made from the thickest material in each 50 tons [45 Mg] of each heat of Grades A, B, D, DS, AH32, AH36, DH32, and DH36, and from each rolled product of Grades CS, E, EH32, and EH36. For flats, rounds, and shapes, one set of three impact tests shall be taken from each 25 tons [25 Mg] of each heat for Grades CS, E, EH32, and EH36, and from each 50 tons [45 Mg] of each heat of Grades A, B, D, DS, AH32, AH36, DH32, and DH36 material. The test results shall conform to the requirements of Table 5.

9.3.3 Toughness test locations, orientations, specimen types, number of tests, and retests shall be in accordance with 9.2.3 through 9.2.7.

9.4 **Rivet Steel and Rivets:**

9.4.1 For rivet steel a sulfur print requirement shall be met when other than killed or semi-killed steel is applied, in order to confirm that its core is free of concentrations of sulfur segregates and other nonmetallic substances.

9.4.2 Test specimens for rivet bars that have been cold drawn shall be normalized before testing.

9.4.3 Finished rivets are to be selected as sample specimens from each diameter and tested hot and cold by bending and crushing as follows: The shank must stand being doubled together cold, and the head being flattened hot to a diameter 2½ times the diameter of the shank, both without fracture. Bend test requirements for rivets are given in Table 6.

TABLE 6 Bend Test Requirements for Rivet Steel

Thickness of Material, in. [mm]	Ratio of Bend Diameter to Thickness of Specimen
¼ [20] and under	flat on itself
Over ¼ [20] to 1¼ [30], incl.	1
Over 1¼ [30]	2

10. **Test Reports**

10.1 When test reports are required by the purchase order, the report shall show the results of each test required by Sections 8 and 9, except that the results of only one set of tests need be reported when the amount of material from a heat in a shipment is less than 10 tons [9 Mg] and when the thickness variations described in Section 9 are not exceeded.

10.2 The thickness of the product tested may not necessarily be the same as an individual ordered thickness since it is the heat that is tested rather than each ordered item.

11. **Marking**

11.1 In addition to the marking specified in Specification A 6/A 6M, all material shall be steel die stamped, marked, or stenciled with its grade designation. Material ordered to cold flanging quality shall be additionally marked with the letter F. When Grades D, DH32, and DH36 are normalized, the material shall be marked DN, DHN32, or DHN36 as applicable. Material ordered to Grade E, EH32, or EH36 shall also be steel die stamped, marked, or stenciled with its slab number.

SUPPLEMENTARY REQUIREMENTS

The following supplementary requirements shall apply only when specified in the order:

S85. Orientation of Tension Test Specimens

S85.1 The orientation of the tension test specimens shall be as specifically stated on the order. (The purchaser shall state whether the tests are to be longitudinal or transverse.)

S86. Orientation of Impact Test Specimens

S86.1 The orientation of the impact test specimens shall be as specifically stated on the order. (The purchaser shall state whether the tests are to be longitudinal or transverse.)

S87. Heat-Treatment of Grade DH

S87.1 Grade DH aluminum-treated steel over $\frac{3}{4}$ in. [19 mm] in thickness shall be normalized.

S88. Additional Tension Tests

S88.1 At least one tension test shall be made from each 50 tons [45 Mg] or fraction thereof from each heat. If the material differs 0.375 in. [10 mm] or more in nominal thickness or diameter, one tension test shall be made from both the thickest and thinnest material in each 50 tons [45 Mg].

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19 Annex III: Principle mechanical characteristics of steel

Hardness: Resistance of a material to a plastic local and superficial permanent deformation

Unit: HV (Vickers), HB (Brinell),
HRC (Rockwell with cone),
HRB (Rockwell with ball),
HK (Knoop)

Tensile Strength: A measurement of the maximum load per unit of original area that a steel has prior to fracture.

Symbol: R_m

Unit: MPa or N/mm²

Yield strength or yield: Stress at which a material starts to deform plastically

Symbol: R_e (Resistance elastic)

Unit: MPa or N/mm²

0,2-Elongation: The yield strength is meant to represent the exact point at which the material becomes permanently deformed, 0.2% elongation is considered to be a tolerable amount of sacrifice for the ease it creates in defining the yield strength.

Symbol: $R_{p0,2}$ (Resistance plastic)

Unit: MPa or N/mm²

Elongation: The permanent extension of a specimen which has been stretched to rupture in a tension test. The percentage elongation is an indication of ductility.

Symbol:

Unit: %

Reduction of area: The difference between the original cross sectional area of a tension test specimen and the area of its smallest cross section. The reduction of area is usually expressed as a percentage of the original cross-sectional area of the specimen. During a tension test this is translated by a very large elongation after passing the maximum tensile strength R_m .

Symbol: Z

Unit: %

Impact value: The rupture elongation (elongation measured from R_m till rupture) is considered to be a measure for the toughness.

The impact test or notch test is a measure for the toughness.

Elasticity: In physics, elasticity is the physical property of a material that returns to its original shape after the stress (e.g. external forces) that made it deform is removed. The relative amount of deformation is called the strain. A material is elastic when relatively little force is necessary to deform elastically f.i. rubber.

High temperature stability: Unwanted carbides and other inter-metallic compounds are only generated at high temperatures

(Critical) cooling rate: The critical cooling rate is the minimum cooling rate at which martensite is formed

Carbide formation: A carbide is an inter-metallic reaction between carbon and a metal. In some cases carbides are desirable to increase the resistance to wear in other cases these carbides are not wanted because they decrease the resistance to corrosion.

Resistance to wear: Wear is the removal of material by friction

Forgeability/Malleability: The forgeability of a metal can be defined as the capability to undergo deformations by forging without cracking

Machinability: Simply defined as a measure of the ease with which a metal can be machined satisfactorily. of brittleness where a material simply breaks upon application of bending force.

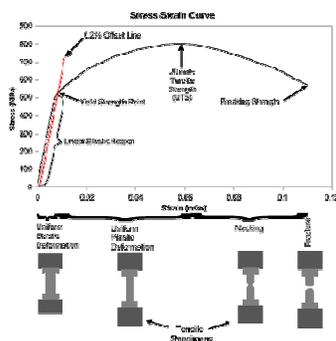
Scaling: Scaling is an oxide layer that appears during the casting process

Nitrability: Degree to which a material can be nitrified. Nitrifying is a heat treatment releasing nitrogen atoms at the surface and creating a hard surface.

Resistance to corrosion

Brittleness: A material is brittle if it is liable to fracture when subjected to stress. That is, it has little tendency to deform (or strain) before fracture. This fracture absorbs relatively little energy, even in materials of high strength, and usually makes a snapping sound.

Ductility: This refers to the property of the material to get deformed before it actually fails due to tension. This property is dependent on temperature and decreases with rise in temperature.

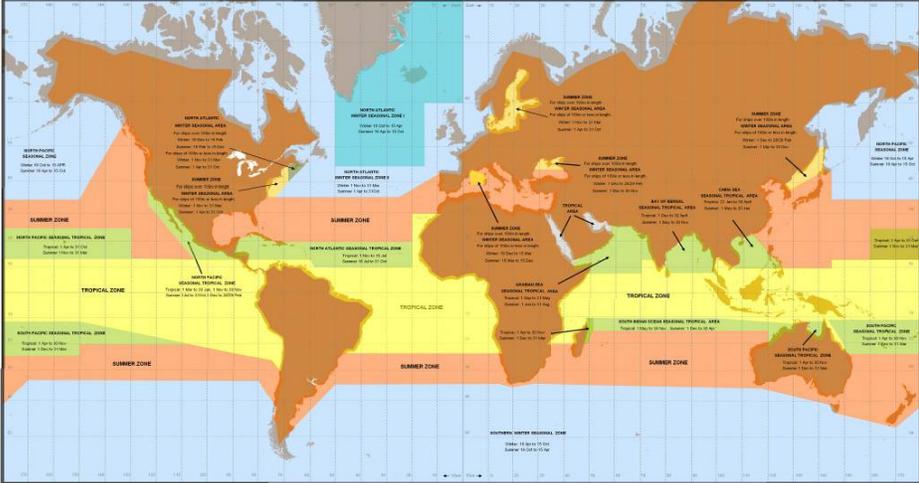


Stress-Strain curve (NDT, 2010) (<http://www.ndt-ed.org/EducationResources/CommunityCollege/Materials/Mechanical/Tensile.htm>)

20 Annex IV: Sample data sheet (versie 2008)

Sample data sheet

Ship's general data

Topic	data
Ship's name	
IMO number	
Ship's type	
Number of loaded voyages per year 2008	(just to know if the ship is making mainly long or short voyages)
Indicate the region most frequented by the ship anno 2008	
Shipping Company	

Expiry date class certificate	
Class Society	
Class notations	
Date of delivery of the ship	
Indicate country of construction	
LOA (in meters)	
BOA (in meters)	
Summer draught (in meters & salt water)	
Main cargo	
Date of last dry dock	
Place of last dry dock	

General data

Topic	Data
Date	
Place (Country + port)	
Name of the observer	
Rank on board	

General Tank Data

Topic	data				
Tank condition	Empty			Partially ballasted	
Tank	Nr.	P/S	%O ₂	%LEL	Toxicity
Tank	Ventilation				
	Yes			No	
Tank	Temp(°C)			Relative Humidity (%)	
Tank	Anodes*			Material/alloy of the anodes	
	Yes	No			
Tank	Try to make a picture of the anodes				
	Condition of the anodes	Good	Fair	Poor	
Tank coating	none	Indicate type of coating			
Date of coating application					
General condition of the tank	Good	Fair	Poor		

% of the time the tank has been dry anno 2008	
Number of times the tank has been ballasted anno 2008	
Time elapsed between last ballast condition and the actual sampling	

Detailed tank data

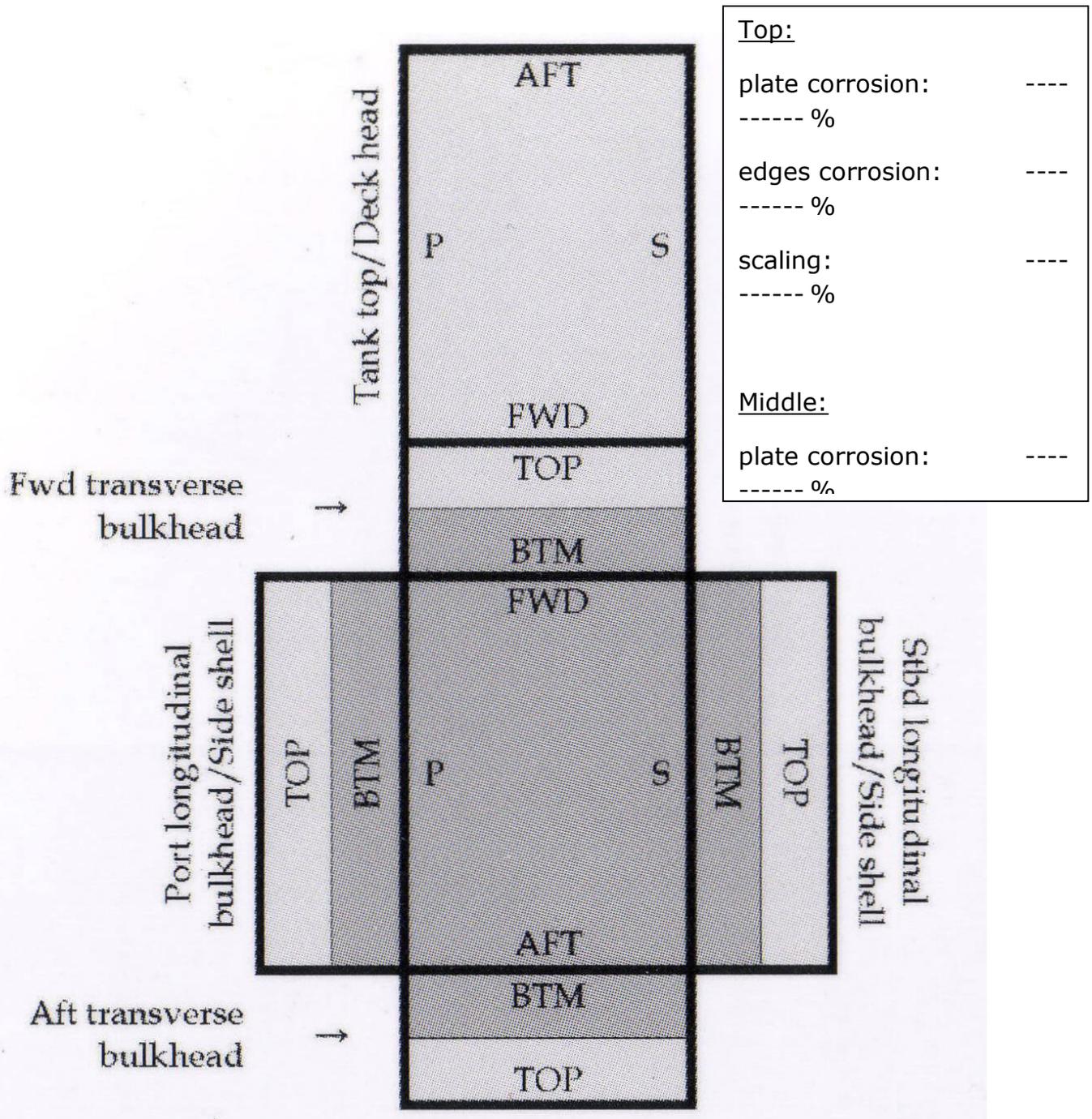
Mark each area with G (Good) , F (Fair) or P (Poor)

Consult Lloyds register tank coating condition guide.

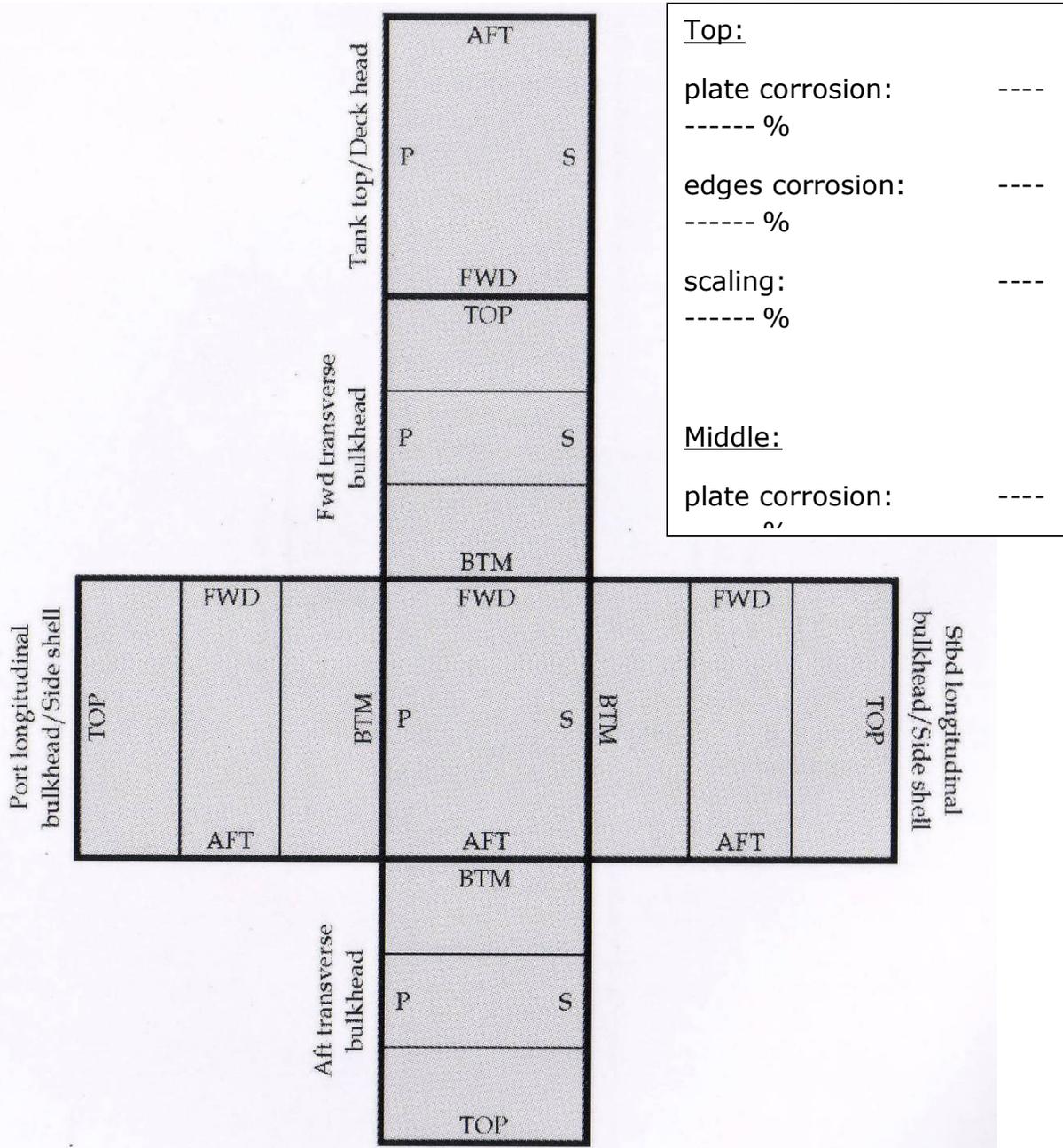
Only fill in appropriate figure.

GOOD	condition with only minor spot rusting affecting not more than 20 per cent of areas under consideration, e.g. on a deck transverse, side transverse, on the total area of platings and stiffeners on the longitudinal structure between these components, etc.
FAIR	condition with local breakdown at edges of stiffeners and weld connections and/or light rusting over 20 per cent or more of areas under consideration.
POOR	condition with general breakdown of coating over 20 per cent or more of areas or hard scale at 10 per cent or more of areas under consideration.

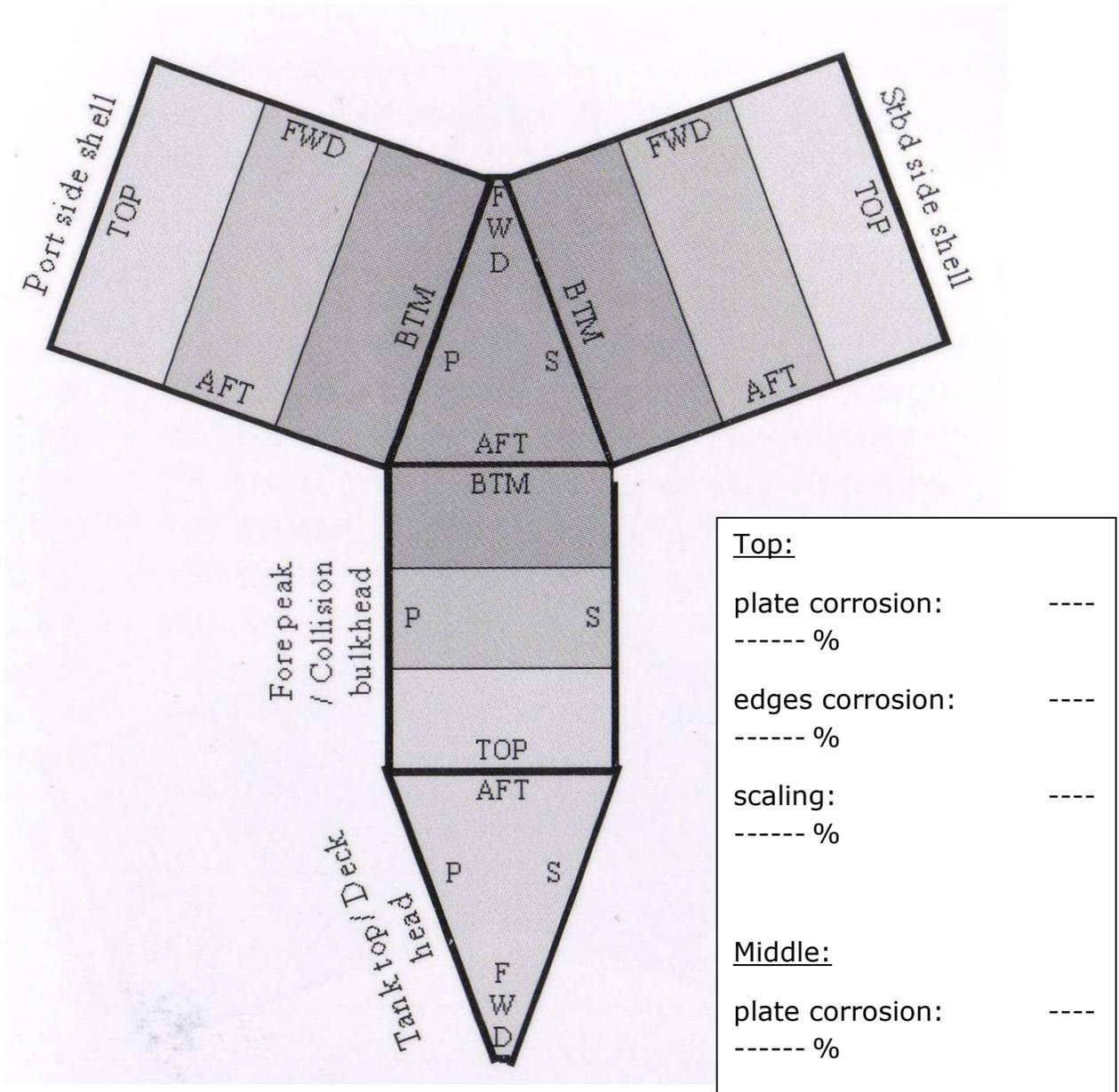
Double bottom ballast tank



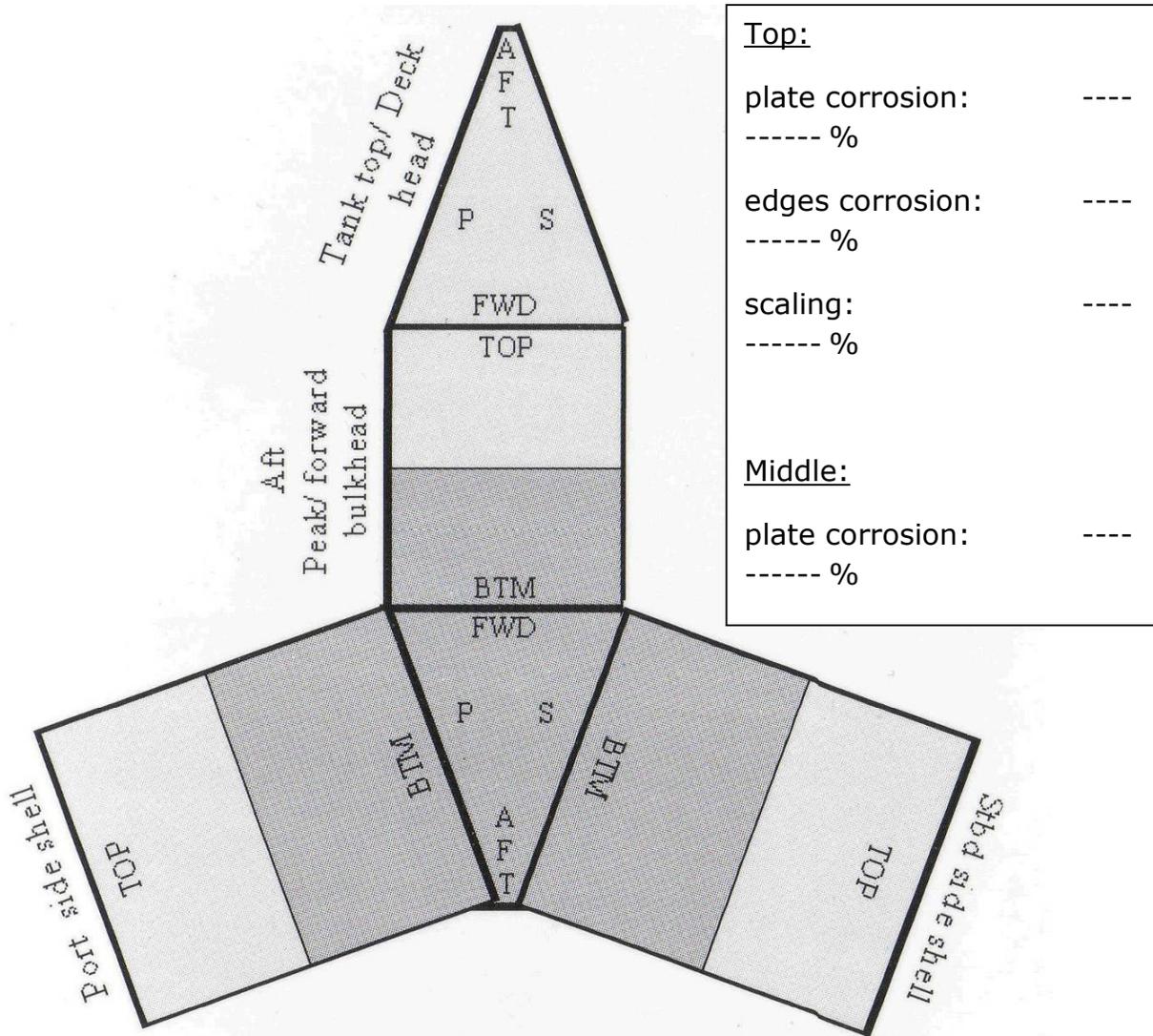
Double hull side tank



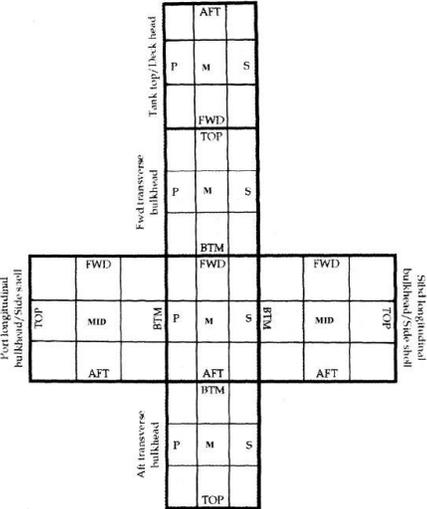
Fore peak tank



Aft peak tank



Sample data – on board

Topic	data			
Sample number	<p style="text-align: center;">- - - / - - - - - / - - -</p> <p style="text-align: center;">(name vessel 3 char. / date (yy/mm/dd) /sample number (00 – 99))</p>			
Photo	Photo inventory nrs.	Per sample at least one photo covering 1m ² meter around the sample place		
Type of sample	Water	Mud	Slime	Rust
	Level the sample has been taken	Top	Middle	Bottom
Indicate where the sample has been taken				

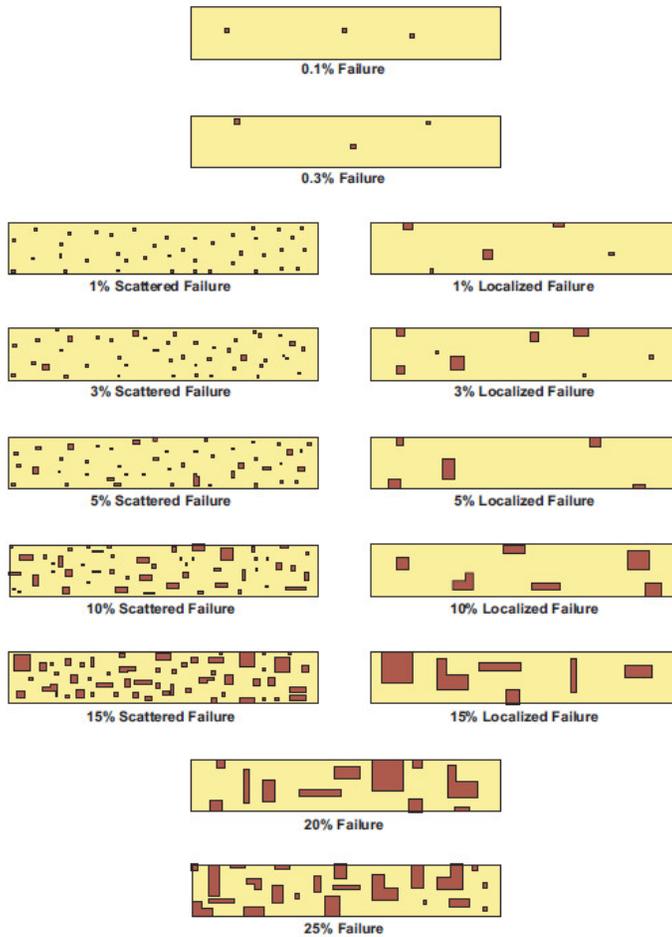
Detailed information on the sampling environment 1 m ²	Plate corrosion (%)	Edges corrosion (%)	Scaling (%)
Detailed information on the sampling environment	Temp H ₂ O	Temp residu	

Sample data – Labo

Chemical sample data	pH	Dissolved oxygen	Conductivity
Chemical sample data	SO_4^{2-}	NO_3^-	S^{2-}
Chemical sample data	PO_4^{3-}	NH_4	NO_2^-
Chemical sample data	Cl^-		
Microbiological data	Sulphate Reducing Bacteria	Iron Reducing Bacteria	Slime Forming Bacteria

Assessment scales for breakdown

Plate



Edges

