06 August 2018

Cargo Tank Corrosion on Tankers

An INTERTANKO Opinion

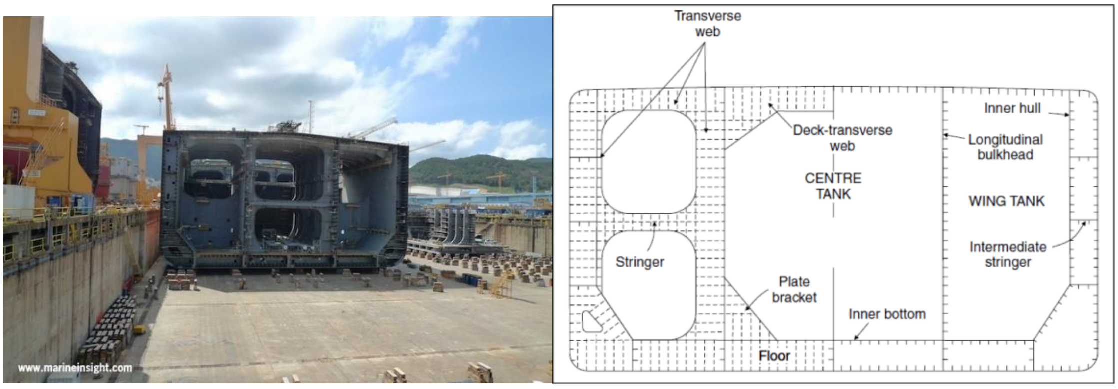
Dragos Rauta, Technical Director

1. Introduction

Since ships are massive steel constructions corrosion is a fact of life. The way corrosion attacks the interior structure of a cargo oil tanker is more insidious because the steel is exposed to corrosive gases, sea water, crude oil and oil products which adds to the harsh environment encountered at sea.

Corrosion in crude oil tankers is nothing new. Traditionally, the internal structure of the cargo tanks was un-coated. Classification Societies' design rules typically incorporate an allowance for corrosion that was based on a certain amount or degree of corrosion. When all tankers were of a Single Hull structure, there was a need for some steel renewal at around the time of the third special survey, i.e. at the age of 15 years.

However, during the latter half of the 1990s, some higher corrosion rates, particularly accelerated pitting corrosion rates have been discovered in the cargo tank bottom plating of a number of relatively new Double Hull crude oil tankers. In some cases such corrosion has taken place within only two to three years of the ship being placed in service.



Cross section of – Double Hull Oil Tanker

Localised pitting to depths of 1.5-3.0 mm has been found, equivalent to an annual pitting corrosion rate of 1.0-1.5 mm, but maximum pitting corrosion rate as high as 2.0 mm per year has been recorded. Some relatively new double hull crude oil tankers have also experienced high corrosion rates at the cargo tank heads at the top of the ullage space.

Discovery of these accelerated pitting rates in cargo tank bottom plating surprised the industry. The high corrosion rates focused attention on a number of factors – including changed operational conditions for crude oil tankers; the "thermos bottle effect" experienced with Double Hull tankers; the use of high-tensile steel (HTS) manufactured using the thermal mechanically controlled process (TMCP steel) and microbial influenced corrosion (MIC).

The causes of this type of corrosion are different to those for tank bottom pitting. Where cargo tank head wastage has occurred, general corrosion rates of approximately 0.1 mm per year are the average which is within normally anticipated. However, in some of the cargo tank heads, the local corrosion rate was 0.15 to 0.25 mm per year, which is approximately 2 to 3 times greater than normally anticipated. The high variation of the main deck temperature between day and night times as well as the humidity in the vapour space introduced by the inert gas system is the main factor of a higher corrosion rate in the ceiling of the cargo oil tanks.

Corrosion process in oil tankers' cargo tanks

In general, aqueous corrosion is the result of an electrolytic process. An electrolytic process needs an electrolyte. The Double Hull structures have an excess of such electrolyte as compared with the single hulls due to higher humidity in both cargo tanks and ballast tanks. The anode is the iron in the steel structure *while the cathode is represented by various other elements including sulphur*. If one of these three basic elements is missing, we can limit the corrosion activity.

One could aim for the removal of the electrolyte, namely the water vapours on the cargo tanks ullage space and the continuous humidity on the ballast tanks. There is nothing one can do to remove humidity from ballast tanks. The percentage of humidity in empty ballast tanks can be as high as 95% depending upon the temperature of the surrounding seawater and cargo temperature in the adjacent cargo tanks. In cargo tanks, water vapours are introduced via the inert gas system. The inert gas, which is produced by flue gas from, for example a tanker's boiler, is both water scrubbed to limit the sulphur content and passes through the water column in the inert gas deck seal before entering the tanks. The water vapour content of the inert gas will depend on the temperature of the flue gas on entry into the scrubber and the extent of condensation of water vapour prior to entry into the cargo tanks. A traditional inert gas system on a tanker has no inert gas dryer or dehumidifier to reduce the water content of the inert gas between the scrubber and the cargo tank. But even with such additional systems, it would appear very difficult to fully control or stop water vapour ingress into the cargo tanks.

The other option is to remove the anode. This means no bare steel, or, in other words, an efficient coating in both ballast and cargo tanks. It is not easy to ensure a good lasting coating but not impossible. The subject will be addressed in the second half of this paper.

This leaves the "cathode" or the main source of the corrosion; the element that wastes the ship's steel structure. There are many elements that could be qualified as "cathode" of the corrosion process in the cargo oil tanks.

Sources for corrosion

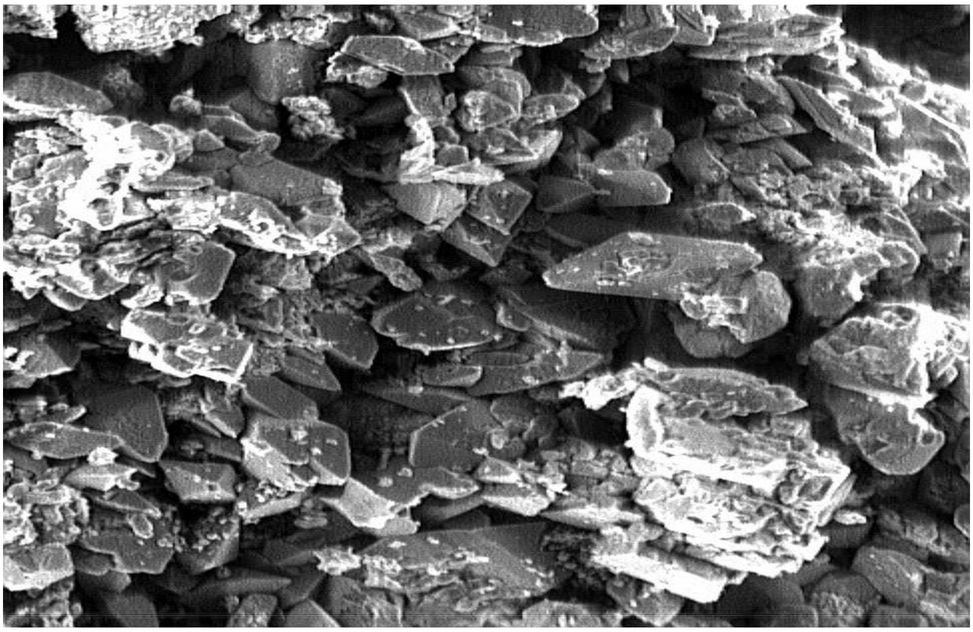
There are many sources of corrosions onboard tankers but one can identify three main types which are specific for oil tankers. These can occur in both cargo and ballast tanks during both laden and ballast voyages. It is noteworthy that these types of corrosion seem to be more aggressive on double hull tankers for reasons already explained.

1. "Sour cargoes" – cargoes with high H_2S concentration

For safety and environmental protection reasons, the maximum amount of oil cargo loaded will fill maximum 98% of the cargo tank volume. Therefore, there will always be at least 2% if not more of the upper part of the cargo tank (also called ullage space) remaining "empty", i.e. containing a mixture of both volatile organic compound (VOC) gases released from the crude oil cargo loaded and inert gas provided by the ship. Therefore, the structure under-main deck area is exposed to such mixture of various corrosive or highly corrosive gases.

Under deck area of a crude oil cargo tank. The greyish coloured deposit on the bulkheads and the internal structures is elemental sulphur. Note the dark black and red-reddish coloured ullage space at the top which is exposed to the inert gas and or VOC during the loaded passage.

One of the corrosive gases that can be released from the crude oil is H_2S, or hydrogen sulphide. More and more crude oils have been found to have high concentration of H_2S. In presence of high humidity, the H_2S breaks down and, as a result of a succession of chemical reactions, ends up as sulphur crystals which have been seen adhering to the under deck structure. These sulphur crystals (observations on board tankers have revealed tons of such crystals) act as a cathode. So, with acid/water droplets from the inert gas, one gets the basis for aqueous corrosion of the ship's steel structure which gets "eaten" away resulting in what we see as rust.



Fully formed Sulphur Crystals as found on rust samples from cargo tanks

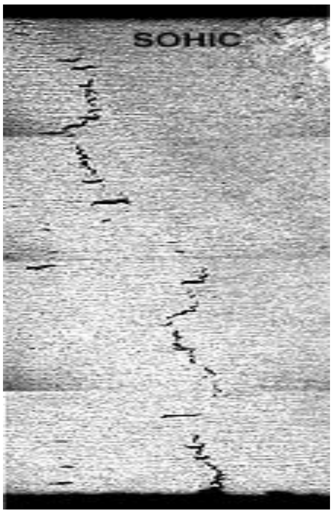
Hydrogen induced cracking - Pyrophoric Iron Sulphide

In addition to this generalised corrosion attack, H_2S will react with Iron Oxide (rust) to create Iron Sulphide (FeS). This process will release some free hydrogen during the reaction whereas the remainder will create water (H_2O). These reaction processes are exothermic, which means that it gives off substantial amounts of heat and thus the term pyrophor, but the whole process is described in some detail within the ISGOTT (International Safety Guide for Oil Tankers and Terminals).

A further reduction occurs when Iron Sulphide comes in contact with oxygen in that it reduces further to pure Sulphur (as has been found adhering to the under deck of tanks) and rust again.

The free or released hydrogen from the first reaction creates another corrosion problem for the deck head structures of the cargo tanks. The deck head structures of a tanker are under the largest loadings for tension and compression being furthest from the longitudinal "neutral axis" of the vessel. Under these circumstances hydrogen will "absorb" into the steel and remain between the crystal boundaries of the steel. This will cause a lamination decay to occur to the exposed steel which is more correctly termed Hydrogen Cracking. Examples of Hydrogen Induced Cracking (HIC) and Stress Oriented Hydrogen Induced Cracking (SOHIC) have been observed and are illustrated below together with the relevant explanation.

Wet H_2S cracking can occur in susceptible steels exposed to aqueous environments containing hydrogen sulphide. It is a form of hydrogen-related cracking and can have two distinct morphologies: The first type is commonly referred to as Hydrogen Induced Cracking (HIC) and can occur where little or no applied or residual tensile stress exists. It is manifested as blisters or blister cracks oriented parallel to the plate surface.



The second type produces an array of blister cracks linked in the through thickness direction by trans-granular, cleavage cracks. The latter type of cracking is referred to as Stress Oriented Hydrogen Induced Cracking (SOHIC). SOHIC can have a greater effect of serviceability than HIC since it effectively reduces load carrying capabilities to a greater degree"[1]

---

[1] INTERCORR INTERNATIONAL – Wet H_2S Cracking – www.intercorr.com

There are three options to fight this type of corrosion:

(a) Remove the hydrogen sulphide from the crude oils prior to loading, which is absolutely impossible.
(b) Remove the sulfur deposits from under the main deck but performing very frequent Crude Oil Washing (COW) which, in addition of removing the sulphurous acid and corrosion products, it may leave a layer of fatty oil film on the steel surface. But frequent COW operations will not meet the environmental expectations due to additional gases releases.
(c) Apply suitable coatings.

2. Carbonic acid

The ullage space will also contain inert gas from the flue gas produced by burning fuel oil in the boilers. The flue gas contains N_2, CO_2, CO and traces of sulphur dioxide. CO_2, in presence of water can form carbonic acid with a pH value of about 4.0 (the inert gas needed for a VLCC with a cargo carrying capacity of 300,000 m^3 can produce as much as 12 tons of carbonic acid during one voyage). This carbonic acid will also remain in the cargo tanks after cargo is discharged as a result of the use of Inert Gas during the discharge programme. We have seen clear evidence of cargo tank bottom corrosion due to carbonic acid. This carbonic acid can also be found in ballast tanks when wind conditions allow. During loading and the laden voyage, released VOCs and inert gas could find their way through the deck vents into the empty and very humid ballast tanks. So, one needs to be aware that the epoxy paints used would need to be able to sustain acidic ambient environments with lower values of pH, below pH4.

The options for protection against this type of corrosion are either a clean inert medium, such as pure N_2, or again an adequate and quality type coating that it designed to meet this environment.

More acidic environment

As mentioned, water enters the ullage space with the inert gas as vapor. During the loaded voyage, if the pressure in cargo tanks required frequent topping up to maintain the cargo tank overpressure, there is steady flow of inert gas and water to the cargo tank ullage space. The temperature in the ullage space will vary with the ambient conditions and day and night changes in temperature. Given the dew point of the vapor, water will condense on the steel surface during the cooler night time periods. The water droplets will contain sulphurous elements and carbon dioxide and will be acidic. Environment with pH as low as one (pH1) has been reported.

Depending on the tanker deck paint color, light or dark it is not unusual to measure a steel surface temperature of 65˚C or more for trade routes frequently travelled by Crude Oil Tankers. This high temperature will accelerate the corrosion rate significantly. Cargo temperature in double hull tankers is some 20˚C higher than in the single hull tankers.

3. Microbial Induced Corrosion (MIC) - Cargo Tank Bottom Plate Pitting Corrosion

Pitting in the bottom plating and on other horizontal surfaces in a crude oil cargo tank is a well-known condition normally encountered when the single hull tanker reached its 3rd and 4th special survey, 15 to 20 years old. Repairs were made by a combination of steel replacement, filling the pits with weld metal, grit blast the tank bottom plate and apply coating.

Some operators have, however, had an unexpected surprise to find, at the first Special Survey of their double hull tankers (i.e. 5 years after the ship was delivered from the shipyard), a very high rate and intensity of cargo tank bottom pitting. The corrosion rates of some of the pitting have been, in the more severe cases, exceeding 1.0 mm per year. If this pitting development were allowed to go un-noticed it would allow crude oil to leak into the ballast tank space. Such a leakage will pose both a potential safety problem and a pollution risk with the crude oil and combustible gases entering a ballast tank.

There are several theorems concerning this question but one of the most popular is that of the corrosion being caused by Sulphate Reducing Bacteria (SRB). These bacteria cause what is known to be Microbial Induced Corrosion (MIC) to the tank bottom plating. This type of corrosion is normally found as deep pitting.

SRB induced corrosion

Microbial induced corrosion is well known to the shore based oil industry and has been so for many years. A wide range of bacteria can exist in all areas of oil production facilities including the production plant, pipelines, the water injection plant, the reservoir and, of course, in the cargo tanks on board the oil tanker used to transport the oil. These microbes produce corrosive acidic compounds. The bacteria most frequently associated with corrosion of steel are those that generate sulphides and these are commonly called sulphate-reducing-bacteria (SRB). Under favourable conditions these bacteria can produce substantial amounts of sulphide which can precipitate out as metal sulphides, dissolved sulphide or hydrogen sulphide.

On board ship, when bacteria find a niche on a steel surface they can proliferate and a corrosion pit develops at the site. Evidence of microbial contamination can be suspected when hydrogen sulphide is detected but is confirmed by the presence of bacteria in water samples taken from the bottom of the tank and the presence of active corrosion pits in the bottom plating.

The environmental conditions preferred by SRB, given that they are anaerobic, include zero dissolved oxygen, water and the presence of soluble organic nutrients. Aerobic micro-organisms use up oxygen and the oxygen deficient zone formed is anodic in relation to adjacent relatively oxygen rich zones thus causing anodic corrosion pits to develop. The double hull acts like a “thermos bottle” and the crude oil cargo cools by convection with the sea much slower in a double hull than in a single hull crude oil tanker. High temperatures, such as those encountered in cargo tanks of double hull tankers, of up to 40˚C and 50˚C give the microbes the opportunity to remain active for much longer than before, provided the necessary nutrients are present which they are in most crude oil tanks.

There are a number of options for repairs of existing pitting and prevent further pitting development. Grit blast the bottom plates and pitting, fill the pits with weld metal or clean and fill the pitting with other filler material, and coat the cargo tank bottoms including the bulkheads to a height of about 1 to 2 meters from the tank bottom with a suitable coating. Such repairs are time consuming and costly for an existing tanker. The application of coating on a pitted but repaired crude oil tank bottom surface may not last for the same period of time as had the coating been applied at the new building stage.

Coated cargo tank bottom

The key issue throughout this analysis is the continuous high humidity in all ballast and cargo tanks as well the preservation of a much higher temperature of the oil cargo. The best remedy is a good paint coating combined with a completely new approach to the preparation of the cargo before loading into the ships.

Coating as a preventive measure

Coating alone stands as the most efficient preventive/anti-corrosive method. Coating is a more proactive measure rather than investing in additional structure with the simple scope of letting it corrode at a rate that, sometimes, is difficult to predict.

Coated under deck with the inspection platform which is a wider stringer with railings

There are some new alternatives developed in Japan and Korea. Nippon Steel and Sumitomo Steel in Japan have published results on new steels with allegedly greater anti-corrosive properties.

However, the practice in the industry shows a large preference in investing in a good coating at new building stage which probably is the best alternative a tanker operator has.

Current legislation

Since July 1st 1998 all new build oil tankers and bulk carriers must have a corrosion prevention system in compliance SOLAS Ch II/1 Reg. 3 –2. But the initial IMO Guidelines for best practices with regard to coating were non-mandatory and their technical content insufficient for a good result.

Consequently, in 2006 IMO has improved the regulation by mandating new Performance Standards for Protective Coatings (PSPC) for dedicated sea water ballast tanks (Resolution MSC.218(82)).

In addition, IMO has amended SOLAS Convention mandating that all under deck and bottom steel plates of the crude oil cargo tanks are coated in accordance with a similar PSCP for crude oil cargo tanks (Resolution MSC.288(87)). The allegedly new corrosive resistant steel was accepted as an alternative.

Main elements of the two PSPCs are:

- Targeted useful coating life of 15 years
- The coating system (epoxy-based) shall be tested, approved and certified based on the criteria given in PSPCs
- Preferably use a lighter colour coating making visual inspection easier
- Application of minimum two stripe coats and two spray coats
- The nominal total dry-film thickness (NDFT) is set to 320 µm with 90/10 rule for epoxy-based coatings
- Strict standards for primary and secondary steel surface preparation
- All material used, activities and conditions under which the coating was performed and the results of the inspection should be included in the Coating Technical File which is provided to the Ship Owner.

It has to be said that the industry has voluntarily started to apply coating in cargo tanks from early 2000s. However, the IMO PSPC has elevated the standards, very much welcomed by tanker owners and operators.

Instead of conclusions

The application of PSPCs in new buildings for sea ballast tanks and more recently on crude oil cargo tanks has been a success story for IMO and for the industry.

So far, the feedback indicates that coatings have been found in good condition even 12 to 15 years after application. There have been repairs to coatings but minimal as compared with experience before application of the IMO PSPCs.

The industry needs to remain vigilant to the quality of coatings and quality of their application as a good job done initially will provide a significant relief in avoiding frequent and very expensive maintenance work and repairs.

However, coatings in the sea ballast water of many ships do have a new challenge though. All ships are now mandated to use systems for treatment of ballast water which should stop movement of aquatic species from one geographical location to a remote one. Many of the Ballast Water Treatment Systems (BWTS) are using active substances and many of these, depending on the type of substances, its concentration and exposure duration may have an adverse effect on the ballast tank coatings. Actually, NACE International has submitted an information paper at IMO's Marine Environmental Protection Committee 64th session (MEPC 64/INF.16 – *Compatibility between ballast water management systems and ballast tank coatings*) providing information on a standard test method NACE has developed to determine the potential corrosion effects of BWTS on the coatings of the ballast tanks.

Since the Ballast Water Convention has entered into force and more and more ships are using BWTS, it might be the appropriate time NACE re-circulates its standard to the entire industry for information and eventual for tests.

Let me finish by making clear that although this paper has provided information on additional challenges on corrosion sources introduced by the double hull design of oil tankers, these are not meant to dismiss the qualities of the double hull design. They serve to illustrate that, as a new conceptual and technical venture, the double hull design for tankers is more complex than one would wish to admit, even more complex than was perceived at inception. However we learn from experience and we correct things as we go along. It is therefore in everybody's interest to keep an open mind and open communication channels on such challenges.