

Performance of stainless steel in marine applications



Introduction

By now it is common knowledge that stainless steels ranging from AISI 316 up to 6Mo and superduplex do not always resist seawater. Crevice corrosion and pitting may develop sooner or later. For example, a 25Cr07Ni super duplex tubular heat exchanger in a marine vessel showed crevice corrosion within 6 month of service. In natural seawater a biofilm will develop on the metal surface and it will always promote the corrosivity of the water. Microbiological Induced Corrosion (MIC) often occurs in seawater. Also galvanic corrosion is a major problem at sea. This article describes the performance of stainless steel in a marine environment, and how the performance can be improved. Materials selection in marine environment strongly gains interest because of the worldwide trend to concentrate

major industrial facilities around sea ports in order to save transport cost and increase cooling capacity.

Materials selection in marine environment.

Piping and static equipment for marine applications can be made out of the following materials:

1. Stainless steel, ranging from 316L, duplex stainless steel to 6% Mo SS. 316L is considered not to be resistive to seawater; the minimum choice is duplex 2205. For that alloy, chlorination of the water is a requirement, and the temperature should not exceed 20 °C (e.g. North Sea). In tropical water with temperatures up to 40 °C (e.g. in Persian Gulf) the minimum requirement for chlorinated water is super duplex stainless steel. Crevice corrosion is a major concern, even for super duplex SS and 6% Mo SS.
2. Use of stainless steel and con-

trolled cathodic protection.

- Under certain circumstances, controlled cathodic protection, such as RCP anodes, works very well for avoiding localised corrosion and galvanic corrosion. By use of cathodic protection, the materials selection can be downgraded, thus saving cost.
3. Use of copper alloys, such as Cunifer and Cupronickel. Only to be used at low flow rates or stagnant water. Erosion corrosion occurs at higher flow rates or in areas of turbulence, e.g. in heat exchangers.
 4. Use of GRP's (Glass Fiber Reinforced Plastics). No corrosion. Not suitable for complicated geometries or constructions such as tubular heat exchangers. May be sensitive to mechanical shock or vibrations.
 5. Use of Titanium. Corrosion does not occur. Hydriding is possible if

- a cathodic protection system or galvanic corrosion polarises the titanium too much. High prices and long delivery time.
6. Carbon steel, uncoated. Without cathodic protection corrosion rate up to 1 mm/year. For internal piping, cathodic protection of carbon steel is no option because anodes distance would be too close for economic CP. Note: For stainless steel internal cathodic protection is an option because the current demand compared to carbon steel is much lower.
 7. Carbon steel, coated. Suitable for the internal of vessels, but not for the internal of piping, heat exchangers and smaller parts.

Corrosion phenomena with stainless steel in seawater.

Localised corrosion

In marine environment stainless steel will never corrode uniformly. Corrosion is localised, i.e.: pitting corrosion and crevice corrosion. Localised corrosion often is being promoted by a biofilm. Picture 1 shows an example of crevice corrosion in a tubular heat exchanger. Crevice corrosion is a major problem in marine environment because of the low resistivity of the water (seawater resistivity is about 0,35 Ohm.m). Even 6% Mo SS at 30 °C can suffer crevice corrosion in seawater. If chlorinated, seawater below 25 °C will not cause pitting corrosion to duplex stainless steel 2205

and alloys with higher PREN-value. PREN value is defined as 'Pitting Resistance Equivalent Number':
 $PREN = \%Cr + 3.3\%Mo X\%N$
 where X = 16 for duplex and X = 30 for austenitic steels. The higher the PREN value the better the pitting resistance.

Stress corrosion cracking

At temperatures above 60 °C stainless steel 304 and 316 are sensitive to chloride cracking. Oxygen must be present, which means that produced water from oil or gas production does not cause stress corrosion cracking, even at high temperature. Duplex stainless steel and 6% Mo are much less sensitive to this phenomena, however under extreme conditions, i.e. high temperature and high stresses and cold deformation it may occur.

Sometimes stress corrosion cracking occurs from the outside, especially longitudinal welded pipes at higher temperature are sensitive to this type of 'corrosion under insulation'.

Galvanic corrosion

Like crevice corrosion, the low resistivity of seawater also promotes strongly galvanic corrosion. Galvanic corrosion is seen as a major concern for materials performance in marine environment. A well known example is bronze bearings in ships, where sacrificial zinc anodes need to protect the steel hull for galvanic corrosion. Also stainless steel can suffer galvanic corrosion, or it causes galvanic corrosion to

other, less noble, alloys.

Five examples:

1. Stainless steel suffers from galvanic corrosion if connected to titanium.
2. If connected to carbon steel, stainless steel will cause galvanic corrosion of the carbon steel. In the same time, the stainless steel parts close to the connection carbon steel/stainless steel will be protected against localised corrosion. In fact the carbon steel parts act as sacrificial anode for the stainless steel parts.
3. Seawater lift pumps and the seawater risers normally are made of duplex stainless steel. The caisson surrounding the pump and riser normally has been made of carbon steel. At height of the narrow crevice between pump and caisson rapid corrosion of the carbon steel will occur, even if the caisson has been coated with a multi layer epoxy coating. The solution in this case is to coat the duplex riser and mount a bracelet zinc or aluminium anode on the duplex riser. Coating the duplex riser will strongly reduce the consumption rate of the bracelet anode.
4. The hull of catamaran ferries has been made of aluminium. The jet itself is a stainless steel construction. The stainless steel may cause rapid galvanic corrosion to the aluminium hull. The solution in this case is mounting aluminium anodes on the stainless steel jet bowl and also insulating the two parts from each other by using PTFE sheets and washers.
5. A cast iron butterfly valve showed extreme rapid corrosion. Failure analysis by Corrodium proved that this was caused by galvanic corrosion. The valve was positioned in a GRE (glass fibre reinforced epoxy) pipe on close distance to a huge duplex stainless steel sea water cooler. The valve was operated by an electrical engine and both the valve and the cooler were grounded. The galvanic current through the ground link was measured at 340 mA! For safety and economical reasons, the ground connection could not be changed and there-



Picture 1: Crevice corrosion in seawater cooler. This corrosion finally leads to leakages.



Picture 2: Position of cast-iron valve compared to duplex SS seawater cooler.

fore the solution in this case was either choice for a stainless steel valve, or installing a sacrificial anode in the GRE pipe (and connecting the anode to the valve. See picture 2 and 3.

The remedy for galvanic corrosion is either arranging electrical insulation with PTFE, or cathodic protection, or both. The first solution not always gives full guarantee to a corrosion free performance and the latter solution requires design by specialists (such as Corrodium bv).

Microbiological induced corrosion

By now it is common knowledge that biofilms are the main force behind corrosion in natural seawater and other natural waters (brackish water, river water, etcetera). Natural seawater is saturated with Oxygen and a normal aerobic biofilm promotes the cathodic corrosion reaction: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$. Thus, the rest potential of the stainless steel will increase and finally the pitting will start with the anodic reaction:

$M \rightarrow Mn^+ + ne^-$

M= Metal, E.g. iron, chromium, nickel and molybdenum.



Picture 3: Severe galvanic corrosion of cast iron butterfly valve due to ground-contact with noble seawater cooler.

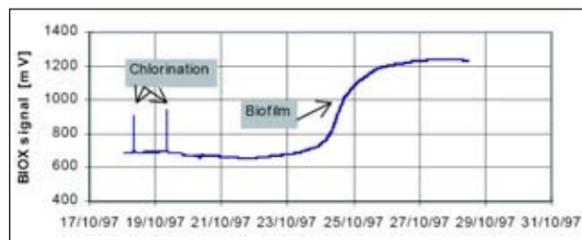
can be illustrated with the BIOX bio film monitor. A stainless steel surface is connected to a zinc anode. A resistor (e.g. 1 Ohm) has been switched between the stainless steel and the anode. The Voltage drop over the resistor indicates the anode current. $100\text{ mV} = 100\text{ mA}$ according to Ohms law. If the biofilm is forming, the potential drop and the anode current will increase, thus proving the current demand of the biofilm. After a badge shot of hypochlorite, the biofilm has destroyed. The potential and current return to original values.

Many microorganism increase the corrosivity of the natural water. However, most notorious are the group of 'sulphate reducing bacteria', SRB's. SRB's are anaerobic bacteria, but often occur in aerobic water because an aerobic biofilm layer covers them. In other words a complex of many microorganism promote each other. Such biofilms cause locally extreme acid environments, with pH values <2 . Evidence for this is the extreme rapid acid corrosion that such biofilms can cause in e.g. duplex stainless steel 2205. Corrodium conducted failure analysis on duplex wastewater piping systems (pH of the water = 7,5, T= 35 °C) where SRB biofilm caused 4 mm wall penetration within 3 month.

Another failure analysis that was conducted concerns buried stainless steel 316L pipelines in a wastewater recovery plant. The internal of the pipelines contained dry air at 80 °C. The external of the pipeline was surrounded by brackish ground water (resistivity 113 Ohm.cm). Ideal circumstances were created for extreme corrosion. The bacteria very much like the warm pipe wall and started acid production to penetrate the pipe wall within 6 months on many places. The appearance of SRB corrosion in stainless steel is very typically. A rust hood, containing metal-sulfides, is formed and below this hood the pH-value can decrease to <3 . Iron-containing acid will drip out of the rusthood and a brown ring of rust deposits is formed around the rust hood.

How to avoid MIC?

1. Chlorination of the water. Note that an over dose of free chlorine also increases the corrosivity of the water. Proper application of the chlorination is very important.



Picture 4: The current demand of a biofilm causes corrosion of stainless steel, but, in the same time also can be used to monitor on biofilm formation. Both the biofilm as the chlorination itself cause a current increase. The mV signal was measured as Voltage drop over a resistance between a stainless steel surface and a sacrificial anode.

Cathodic protection decreases the rest potential back in the safe passive area and thus cathodic protection helps to avoid MIC and localised corrosion.

The current demanding properties of a biofilm



Picture 5: A rust hood, containing iron sulfide and caused by MIC.



Picture 6: After removal of the rust hood, extreme acid attack was noted. The brown deposited rust ring, indicates the former borders of the rust hood. Clearly can be seen that only a strong acid, such as hydrochloric acid, can cause this type of etching of the surface.

2. Flash temperature treatment of the water. Above 60 °C MIC will not occur.
3. Cathodic protection. Cathodic protection prevents corrosion, but also influences chemistry, among which pH value, on the metal surface. Currently scientific experiments are being done to get a better understanding of the relationship between polarisation and biological growth on surfaces.

Cathodic protection of stainless steels.

Most corrosion problems with stainless steel in marine environments can be avoided by use of cathodic protection. Both 'supressed current' and sacrificial anodes can achieve. The latter mentioned method normally is beneficial because it is more economical and less sensitive to failure.

The current required for protecting the stainless steel only is a couple of mA/m², compared to ~25 mA/m² for carbon steel. Carbon steel needs to be protected against uniform corrosion and therefore needs this high current, where stainless steel only needs to be polarised some 100 mV to keep the potential below the pitting potential in the safe 'passive region'.

If sacrificial anodes were connected to stainless steel, the current would be too high resulting in fast anode consumption and hydrogen charging of the stainless steel. The latter may lead to hydrogen embrittlement of duplex stainless steel, titanium (hydriding) and

ferritic/martensitic stainless steels. For that reason, the anode current needs to be controlled by a resistor (RCP anodes) or a diode. Proper cathodic protection design is required to assure best performance.

External atmospheric corrosion.

If uncoated, 316L piping and especially tubing suffer from rust formation and pitting, leading to leakages. Also pitting corrosion and chloride cracking, at temperatures above 60 °C, occur under insulation material, provided it gets wet. For that reason, coating of the outside is recommended for piping. Materials selection for tubing normally is 6% Mo SS, which is resistant to corrosion from the outside. For the rest all uncoated 316 materials, such as instrument housing, will start to rust.

Conclusions

1. Stainless steel performance in seawater is good provided that proper precautions are being made and provided the proper alloy is being selected.
2. Because of (micro)biological activity and formation of a corrosive biofilm, natural seawater is significantly more corrosive than properly chlorinated seawater.
3. Cathodic protection improves performance of stainless steel in seawater and brackish water.
4. For 316 stainless steel, also severe atmospheric corrosion and corrosion under insulation may occur from the outside. The outside of the piping needs to be coated and the advised materials selection for tubing is 6% Mo SS.

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Jan Heselmans graduated from PolyTechnical Highschool in Utrecht in 1986 and since is active in materials and corrosion engineering, research, failure analysis and innovations related to materials performance and corrosion. He worked for HMC-Corlab, CorrOcean, Force Technology and currently is employed by Corrodium bv.

Corrodium bv (www.corrodium.nl), est. in 1989, is an expertise and development centre for materials performance in upstream oil and gas, offshore and marine environment and industrial applications. Corrodium bv participates in several international projects for improving materials performance under severe conditions.