Accelerated crevice corrosion testing of 6Mo stainless steel flanges with different gasket materials in seawater

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Summary

Crevice corrosion has long been the Achilles heel of stainless steel in seawater service. Over the years, we have come across a huge number of instances of premature leakage in piping systems caused by crevice corrosion. This corrosion phenomenon turns out to be the determining factor in the practical lifetime of many seawater piping systems. The present study describes an accelerated electrochemical testing approach that was established to simulate failures observed in a firewater system. Flanges of type 6Mo stainless steel were subjected to slow stepwise polarisation in artificial seawater at 22±2 °C. Subsequent polarisation to +300 mV SCE showed whether repassivation or propagation could be expected under conditions representing marine biofouling. The performance of three types of gasket materials was compared and correlated with the failures. A distinct difference in behavior was observed between the tested spiral wound graphite and polymer gaskets, the graphite gasket being inferior. Based on the study, different aspects related to crevice corrosion are discussed; i.e. gasket setting, biofouling and preventive measures based on e.g. RCP.

1 Introduction

Crevice corrosion has long been the Achilles heel of stainless steel in seawater service. Over the years, we have come across a huge number of instances of premature leakage in piping systems caused by crevice corrosion. This corrosion phenomenon turns out to be the determining factor for the practical lifetime of many seawater piping systems.

The present study was motivated by failures observed in a firewater system on a offshore oil and gas production platform in the north sea. The firewater is essential since no oil or gas can be produced without firewater coverage. According to the actual piping spec stubend flanges of type 6Mo were assembled with duplex stainless steel spiral wound graphite gaskets.

Severe crevice corrosion and leakages were observed in several flange couplings within one year. The media in the affected fire water system was stagnant seawater at ambient temperature most of the time. A failure analysis of 20” blind flanges was carried out, Figure 1. This study indicated that corrosion was caused by the less resistant duplex material being used for the spiral in the graphite gaskets. At the same time, metallurgical defects or material mix-up were eliminated as possible causes of corrosion.

Graphite gaskets are generally regarded as unsuitable for seawater systems due to its noble galvanic properties [1]. The NORSOK M-001 standard [2] and other oil company standards generally advise against using graphite gaskets for seawater systems, whereas such gaskets are suitable for systems operating at high temperature, e.g. steam or hot oil. However, the exact mechanism related to the unsuitability of graphite in seawater is not clear.

Turnbull has carried out electrochemical studies on graphite gaskets in order to obtain data for mathematical modelling of crevice corrosion [3]. This study indicated that graphite gaskets could have both a beneficial and a harmful effect on crevice corrosion depending on the service conditions. At normal conditions involving marine biofilm formation, the graphite inside the crevice might increase pH due to the low overvoltage for hydrogen evolution. This prevents initiation of crevice corrosion. On the other hand, under strongly oxidizing conditions caused by chlorination, graphite contributes to the development of corrosion.

In the present case, the crevice corrosion in the flanges presumably developed under moderately oxidizing conditions in stagnant seawater where graphite gaskets are supposed to be beneficial according to Turnbull. Consequently, other parameters such as gasket design and tightening may have been more decisive for the development of corrosion. One obvious issue is the use of a standard duplex spiral in the graphite gasket as this material is inferior to 6Mo in seawater.

In order to support the selection of new gasket materials, a series of corrosion tests were performed including both the original graphite gasket and two candidate gasket materials.

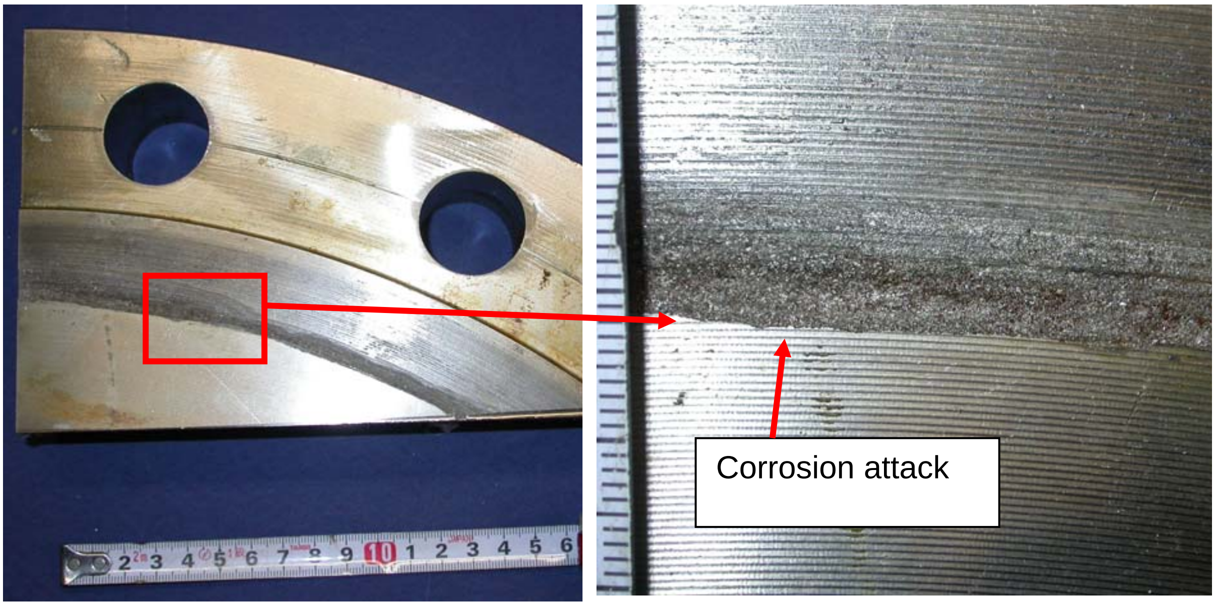


Figure 1: Failure investigation of crevice corrosion in 6Mo flange after 1 years of service in a firewater system.

The experimental approach was inspired by our participation and the results of the CrevCorr project, which aimed at establishing a standardised method for crevice corrosion testing of CRAs in seawater [4]. We have used a similar approach for crevice corrosion testing of stainless steel connections in drinking water [5].

2 Experimental technique for electrochemical corrosion testing

Based on the failure analysis, the following approach for the tests was established. A test set-up as shown in Figure 2 was built from 2” 6Mo stub ends. The exposed surface area of the cell was approx. 160 cm^2.

Each test was carried out as follows:

1. The stub ends are degreased in ethanol. Gaskets are inserted as-delivered without additional cleaning.
2. The cell is assembled and tightened to the prescribed momentum with a calibrated torque wrench.
3. The cell is put under vacuum and filled with artificial seawater (ASTM D1141). This procedure ensures rapid entrance of solution in the crevice.
4. The open potential (OCP) is measured for 24 hours.
5. The sample is slowly polarised in steps from the corrosion potential until initiation of corrosion at a rate of 25 mV every six hours. The criterion for corrosion is when the total current exceeds 5 mA.
6. When corrosion initiates, the potential is lowered to +350 mV Ag/AgCl and kept here for about 24 hours to study propagation or repassivation.

Two tests were run in parallel for each set of gaskets at the test temperature of 22±2°C. Table 1 summarises the parameters of the performed tests.

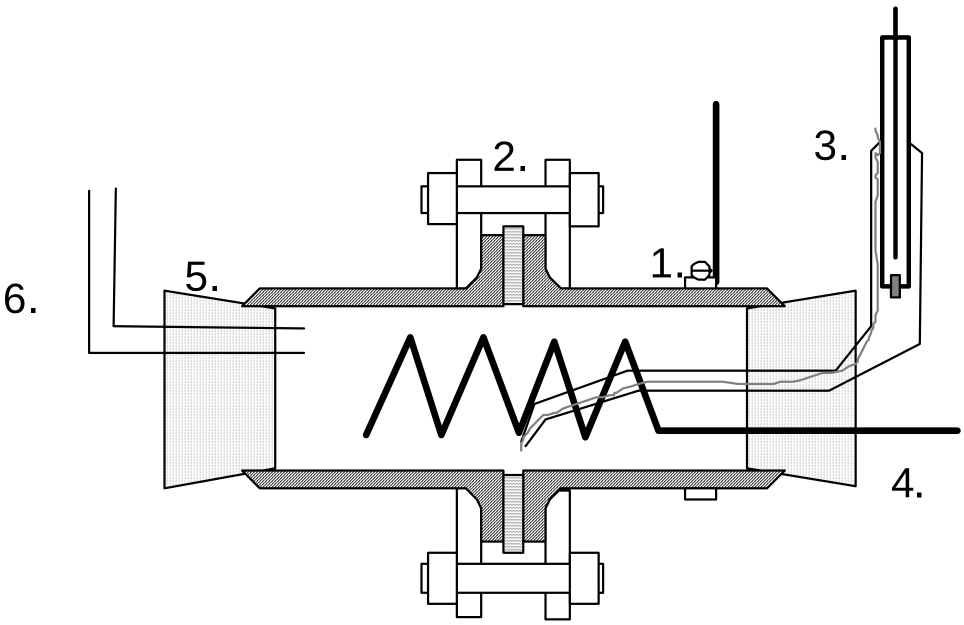


Figure 2: Test set-up: 1. Stub end 2”, 6Mo, electrical contact at hose clamp. 2. Flange and gasket. 3. Reference electrode (Ag/AgCl/sat.KCl) in salt bridge with cord to avoid air bubbles. 4. Hastelloy C276 counter electrode. 5. Silicone rubber stopper. Zinc oxide paste is applied at contact face to prevent crevice corrosion. 6. Filling tube.

Table 1: Tested gasket materials and parameters.

Gasket material	Tightening
Graphite, spiral wound, duplex 2205 spiral	5/8" bolts, 122 Nm
Flexitallic FRG	5/8" bolts, 106 Nm
Klingersil C-4430	5/8" bolts, 63 Nm

3 Results

Examples of the obtained current/potential curves are shown in Figures 3 and 4.

The initial measurement of the corrosion potential shows a level between -100 and +20 mV Ag/AgCl after the first 24 hours of exposure. The highest potentials are observed for the graphite gaskets as expected due to its noble properties.

The obtained polarisation curves show a distinct difference between the graphite gasket and the two polymer gaskets.

The graphite gasket tests show a slow increase in corrosion current starting at +100 to +200 mV Ag/AgCl. The curve breaks at about 1 mA, which roughly corresponds to the typical current criterion of 10 µA/cm^2 for reading off the breakdown potential. At this point, the potential is +750 mV Ag/AgCl in the first run and +400 mV Ag/AgCl in the second run. In both tests, corrosion propagates at same rate after lowering the potential to +350 mV Ag/AgCl at the end of the test.

The FRG gasket tests show a corrosion current close to nil at potentials up to about +800 mV Ag/AgCl. The corrosion current of 1 mA is exceeded at +1050 and +1025 mV Ag/AgCl for runs 1 and 2, respectively. In both cases, corrosion stops immediately after lowering the potential to +350 mV Ag/AgCl at the end of the test.

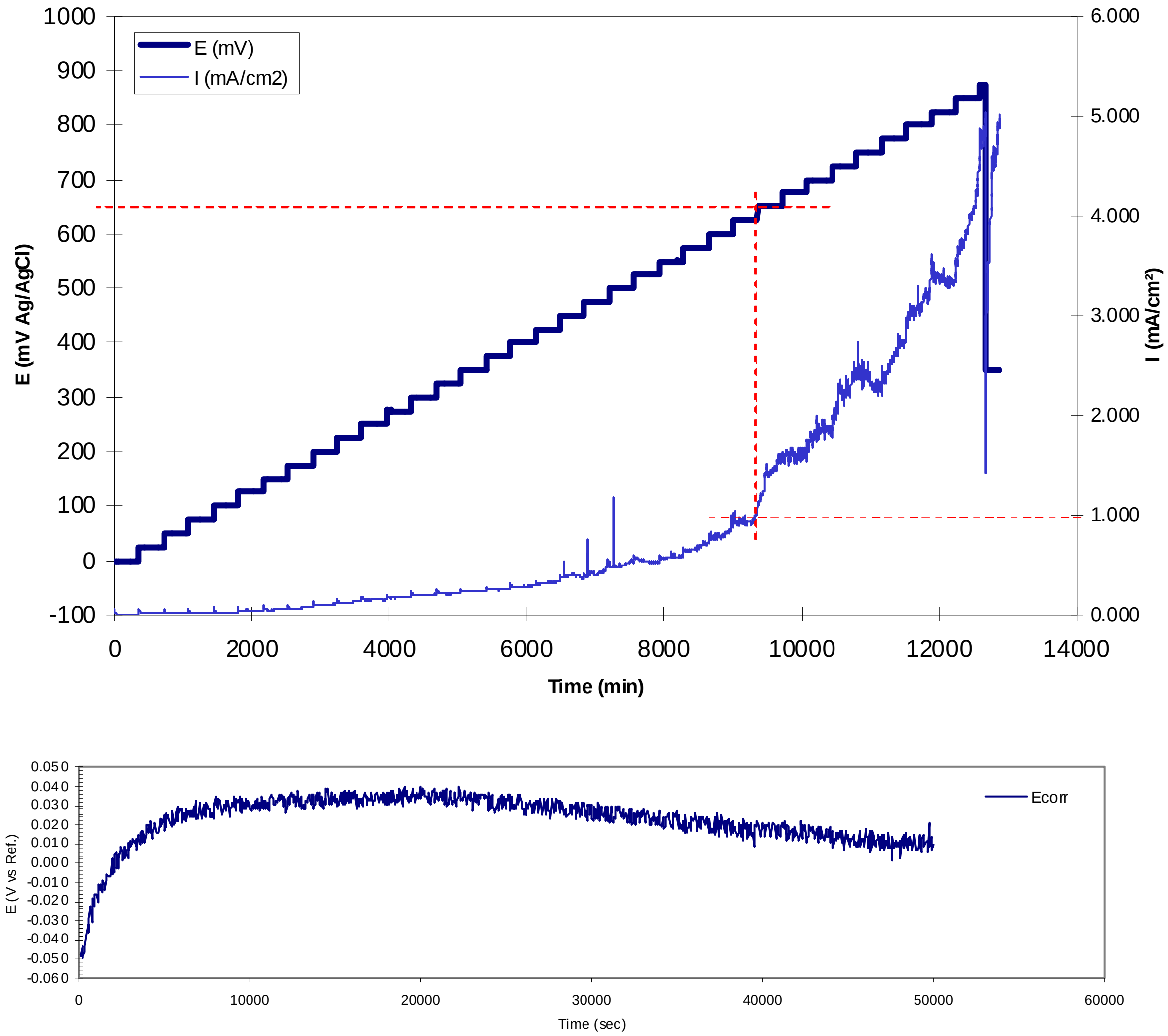
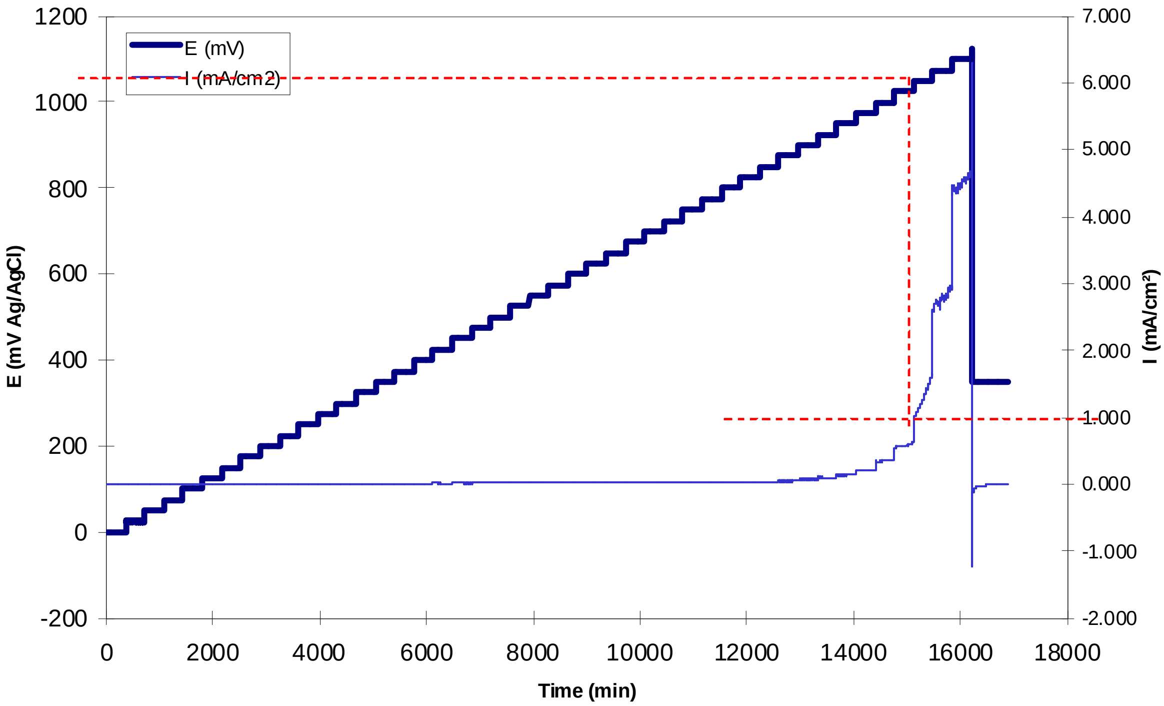


Figure 3: Current and potential measurements of graphite gasket. Corrosion initiates at +750 mV Ag/AgCl. Curve at the bottom represents potential measurement prior to polarisation.

The Klingersil gasket tests show a behaviour similar to that of the FRG gaskets tests. The corrosion current is close to nil at potentials up to about +900 mV Ag/AgCl. The corrosion current of 1 mA is exceeded at +1050 and +1075 mV Ag/AgCl for runs 1 and 2, respectively. In both cases, corrosion stops immediately after lowering the potential to +350 mV Ag/AgCl at the end of the test.

A comparison of the obtained initiation potentials and observed propagation behaviour is shown in Table 2.

Subsequent to testing, all parts were inspected for corrosion. In addition, half of the stub ends were sectioned lengthwise to examine the interior pipe surface. In all cases the samples were free from pitting on the interior pipe surface including the crevice area at the rubber stoppers.



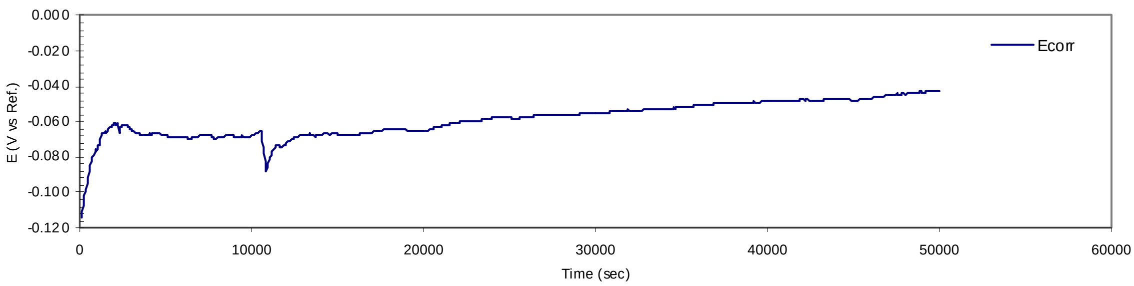


Figure 4: Current and potential measurements of FRG gasket. Corrosion initiates at +1050 mV Ag/AgCl. Curve at the bottom represents potential measurement prior to polarisation.

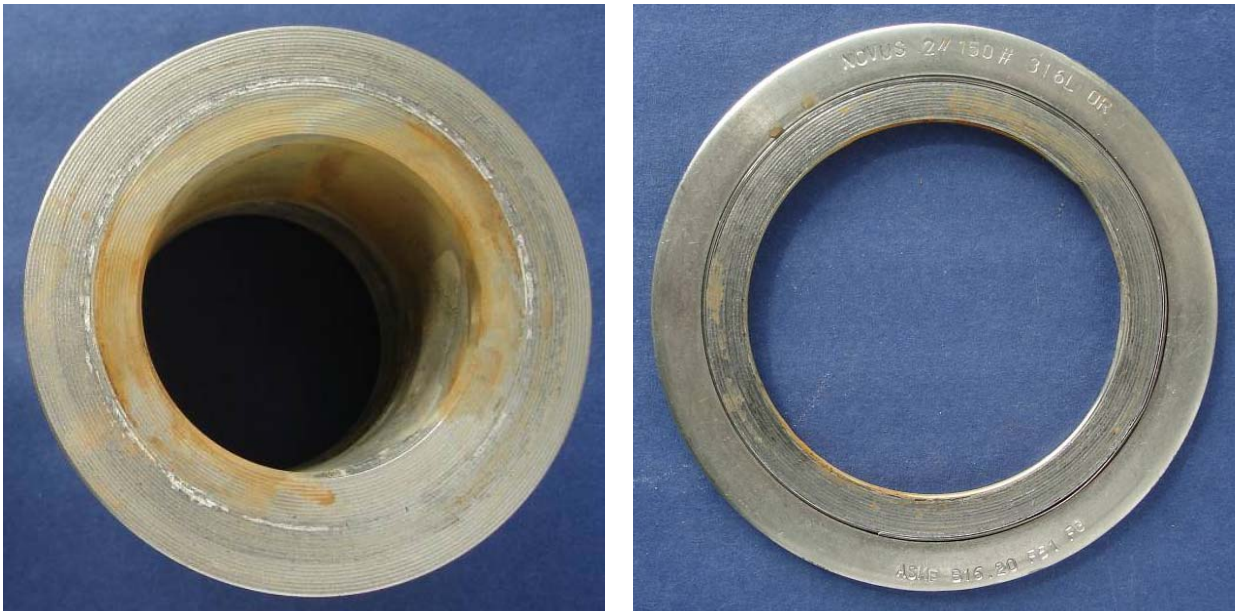
The parts from the graphite gasket tests showed the most distinctive corrosion attacks. In both cases, the duplex spiral suffered severe corrosion; especially at spot welds at the end of the spiral and along the outer windings. In addition, corrosion could be seen on the outer 2-3 mm of the covered part of the 6Mo flange.

The flange parts from the FRG and Klingersil gasket tests showed the only superficial corrosion attacks. As the behaviour in these tests was almost identical, it is likely that the detected current is related to transpassive corrosion rather than localised corrosion such as pitting and crevice corrosion. The observed corrosion was, in all cases, limited to superficial etching in the outer part of the covered flange.

Examples of the observed corrosion on the parts are shown in Figures 5 to 9 and summarised in Table 2.

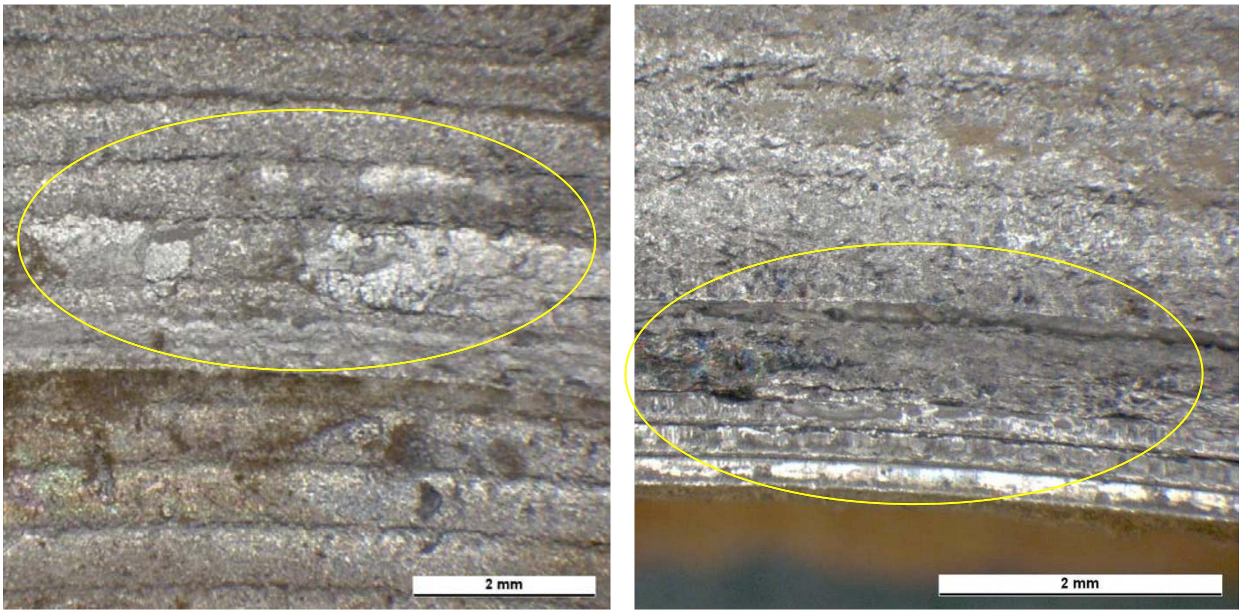
Table 2: Summary of the test results.

Gasket material	Run	Initiation potential mV Ag/AgCl	Propagation at +350 mV Ag/AgCl	Observed corrosion
Graphite, spiral wound	1	+750	Yes, up to 5 mA	Corrosion in duplex spiral, especially at spot-welds at the end of the spiral, and on the outer windings. Corrosion on the outer 2-3 mm of the covered part of the 6Mo flange. No pitting on free faces.
	2	+400	Yes, up to 5 mA	
Flexitallic FRG	1	+1050	No	Superficial corrosion in mouth / outer part (1 mm) of crevice. No pitting on free faces.
	2	+1025	No	
Klingersil C-4430	1	+1050	No	Superficial corrosion in outer part (0-5 mm) of crevice. No pitting on free faces.
	2	+1075	No	



a. b.

Figure 5: Overview of flange face (a) and graphite gasket (b) after test.



a. c.

Figure 6: Close-up of superficial corrosion in outer grooves on 6Mo flange face (a) and deeper corrosion along edge in outer windings of duplex spiral in the graphite gasket (b).

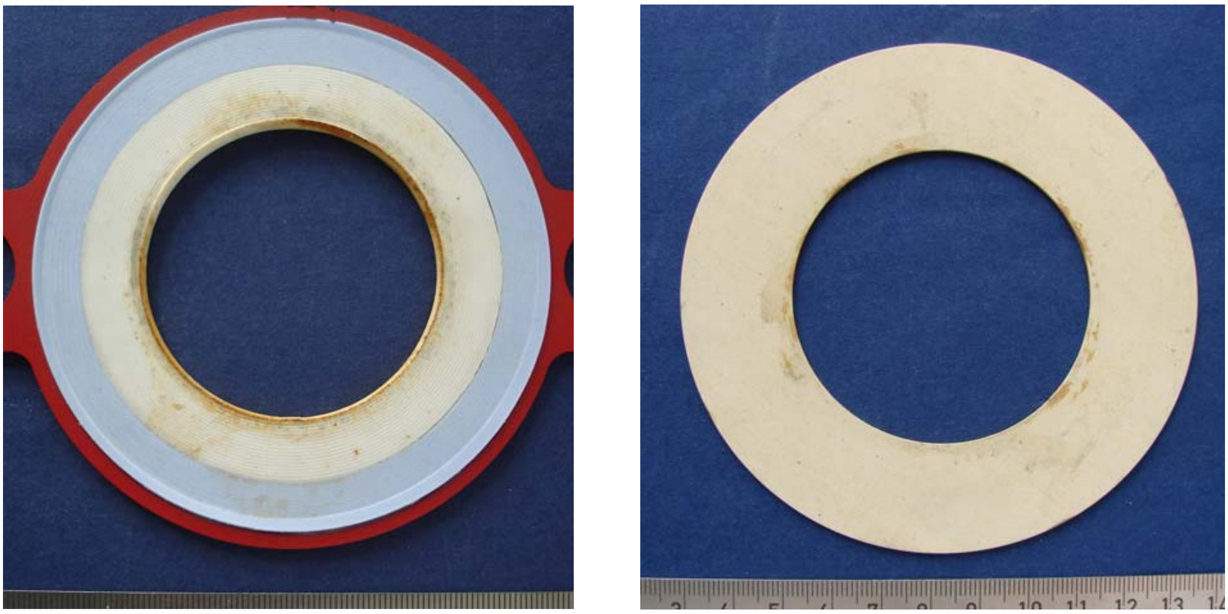


Figure 7: Overview of FRG gasket (left) and Klingersil C4430 gasket (right) after test.

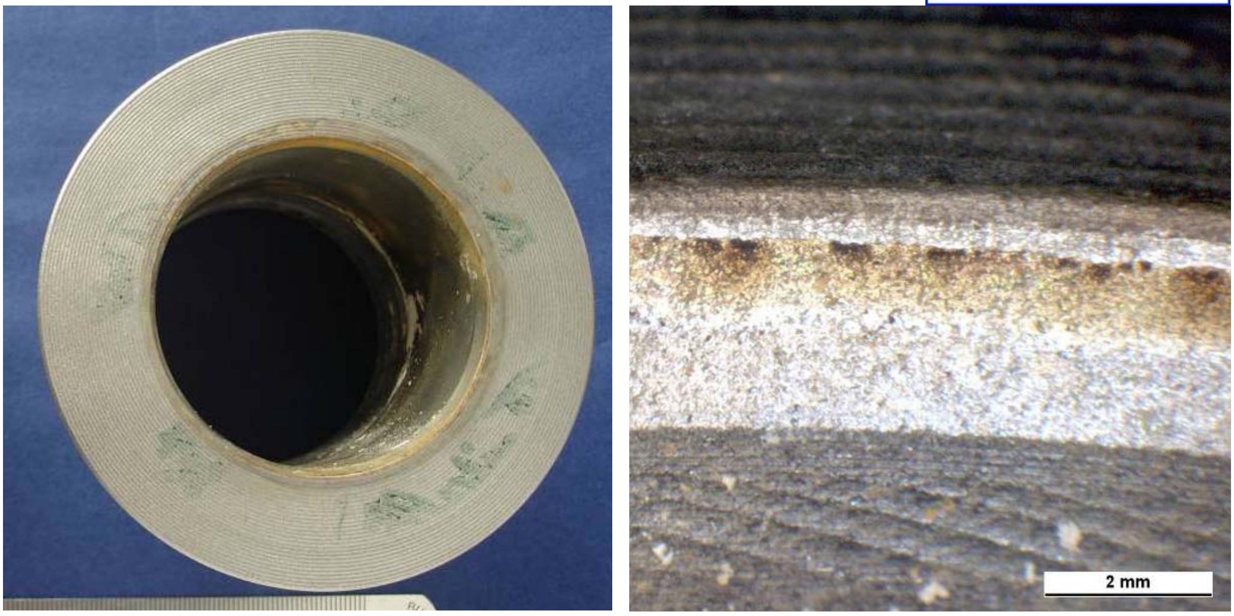


Figure 8: Overview of flange face from the FRG gasket test (left). Close-up of superficial corrosion on flange face (right).

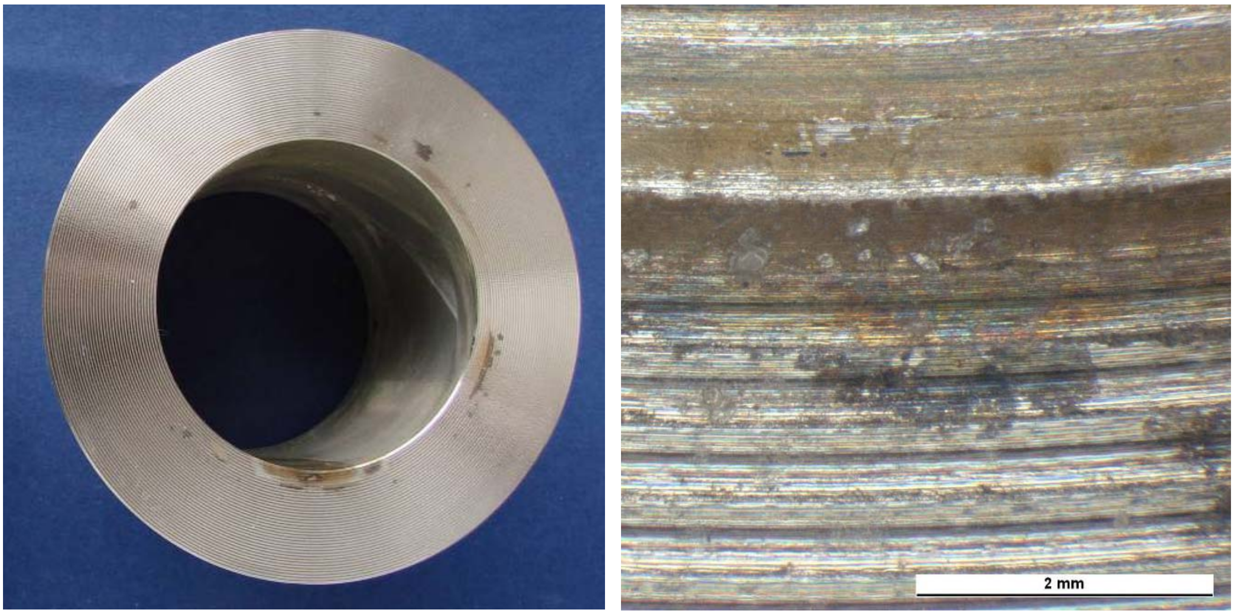


Figure 9: Overview of flange face from the Klingersil C4430 gasket test (left). Close up of superficial corrosion on flange face (right).

4 Discussion

The typical corrosion potential of a passive stainless steel in non-chlorinated, natural seawater is +350 to +450 mV Ag/AgCl. To a great extent, this potential is determined by the formation of a marine biofilm which causes ennoblement, i.e. more oxidizing conditions than those observed in sterile water. For the “fire ring main” in question, we expect a potential of this magnitude because no chlorination is applied in this system.

Chlorination is often performed in other seawater systems to avoid marine biofilm formation as well as settlement of marine organisms that might plug filters, nozzles, etc. Depending on the chlorination pattern the resulting potential could be either higher or lower than the above-mentioned level. Continuous chlorination to a level above 1 ppm free chlorine typically results in a potential of +600 mV Ag/AgCl. Intermittent or low chlorine dosage typically leads to a potential with peak values of +400 mV Ag/AgCl, i.e. overall less oxidizing conditions than that of the non-chlorinated system. Since the risk of corrosion increases with potential, the latter application method is usually considered most favourable to avoid corrosion.

When correlating the above potential levels with the obtained test results, it appears that the graphite gasket is in the risk zone, since corrosion may initiate at +400 mV Ag/AgCl (or possibly lower). Moreover, rapid propagation of corrosion is observed at +350 mV Ag/AgCl subsequent to initiation. Consequently, the obtained test results correlate well with the observed failures in the fire water system.

The observed initiation potentials for rapid corrosion of the polymer gaskets (FRG and Klingersil) are well above this potential level. In fact, it was not possible to develop critical, localised corrosion at potentials below the point where transpassive corrosion occurs. In contrast to the graphite gasket test, no corrosion was observed subsequent to initiation when lowering the potential to +350 mV Ag/AgCl. On this basis, we consider the FRG and Klingersil gaskets as equal in respect to prevention of crevice corrosion.

From the performed tests it appears that initiation and propagation of crevice corrosion occur at a much earlier stage for the graphite gasket when compared with the polymer gaskets. The observed corrosion in the graphite gasket tests can be ascribed to the use of the less resistant duplex grade for the spiral. Corrosion is still observed on the highly resistant 6Mo grade, but we interpret this as secondary damage from the corrosion originally initiated on the duplex spiral. This view is also supported by the results of the polymer gasket tests, which showed no severe corrosion. With these types of gaskets, we do not expect crevice corrosion of 6Mo flanges at temperatures below 35-40 °C in seawater. We base this assessment on our experience from other tests and literature.

In similar testing of graphite gaskets with 6Mo spirals it would have been interesting to study the effect of graphite more closely, but such gaskets were not available. Nevertheless, graphite gaskets are not intended for seawater service, but were originally developed for high temperature systems such as steam, hot oil or corrosive chemicals. Unintentional use of graphite gaskets in seawater with CRAs have been reported frequently in the past, but today this issue is addressed by e.g. the NORSOK standards [2].

Apart from the gasket material, flange tightening and gasket setting also affect the risk of crevice corrosion. Ideally, the two abutting flange faces are kept closely together by a clamping force with a gasket in between. If a sufficiently high contact pressure is established, and if the gasket material is sufficiently impermeable to water, there will be no water-filled crevice and hence no crevice corrosion. This situation has been obtained in the present study by carefully applying the prescribed momentum using a calibrated torque wrench. However, the gasket material may

suffer a permanent set over time thus reducing the contact pressure and hence the sealing capacity. Consequently, retightening or complete disassembly/reassembly may be needed at regular intervals depending on the gasket setting properties.
By this, premature corrosion attacks may be detected and, in many cases, the calamity can be remedied by use of solvent-free epoxy products with metallic zinc filler.

In seawater cooling systems with temperatures up to 45 °C, it is possible to combat crevice corrosion by use of highly corrosion-resistant alloys such as 654 SMO or nickel alloys; either as flange base metal or as overlay-welded surface layers. The inherent corrosion resistance is high enough to prevent onset of crevice corrosion, but for other flange materials from ordinary stainless steel up to super austenitic steels (6 SMO, AL-6XN, etc.) and super duplex steels (SAF 2507), there will be a risk of crevice corrosion attacks in flange joints. This risk may even increase with the use of biofouling control by use of chlorination depending on the application pattern.

Another viable solution is internal cathodic protection by the RCP system, i.e. resistor controlled protection. It has a merit in combating internal corrosion problems in stainless steel piping systems, but it works best in connection with an effective anti-biofouling treatment that keeps the surfaces free from biofilm and marine growth which would otherwise consume the protective current in the RCP system. The RCP system has a long record of successful use [6]. When installed and operated correctly, one anode may protect long distances with anode lifetimes up to 30 years.

Going back some 30 to 40 years, crevice corrosion in AISI 304 and 316 was successfully combated by use of leaded paste in combination with asbestos-containing gaskets. There were also successful attempts to incorporate metallic lead in the gaskets. As use of lead was later banned, it was substituted by zinc oxide. In Denmark we used petrolatum (Vaseline) with 20 % zinc oxide, which was also widely used as an ointment for treating rash and skin eruptions in baby bottoms. Zinc oxide-containing paste is still in use in Denmark but with the introduction of the more corrosion-resistant stainless steel alloys, it is perhaps less common today.

We have previously (20 years ago) conducted crevice corrosion tests with AISI 316 during which zinc oxide-containing compound was applied to ordinary rubber-fibre gasket surfaces and in crevices in flanges, pumps and valves in seawater cooling systems. This proved capable of preventing crevice corrosion in the time span between plant shutdown (up to 2 years). It is believed that the presence of zinc ions inside the crevice prevents the solution pH from becoming acidic and hence prevents onset of accelerated corrosion. By securing a certain buffer capacity of zinc ions, the corrosion protection may be retained for very long periods, probably outliving the pipe system. New tests have been initiated looking into ways of doping surfaces of gaskets etc. with zinc compounds. The purpose of these tests is to determine the long-term effect and the longevity of the crevice corrosion combating treatment.

5 Conclusion

An electrochemical test technique was established in order to study the effect of different gasket types on the risk of crevice corrosion of 6Mo stainless steel in seawater. Three types of gaskets were tested in double in artificial seawater at 22 °C, i.e. graphite spiral wound, FRG and Klingersil C-4430 gaskets.

Initiation and propagation of crevice corrosion was observed in the graphite gasket test at the potential level occurring in natural, non-chlorinated seawater gaskets, i.e. +350 to +450 mV Ag/AgCl. The observed corrosion can be ascribed to the use of the less resistant duplex grade for the spiral, but also secondary corrosion on the 6Mo flange took place.

The tests with polymer gaskets (FRG and Klingersil) showed no corrosion at potentials up to about +1050 mV Ag/AgCl. Immediate repassivation occurred after lowering the potential to +350 mV Ag/AgCl at the end of the test. Consequently, the FRG and Klingersil gaskets are considered equally suitable to prevent crevice corrosion.

Graphite gaskets are generally regarded as unsuitable for seawater systems due to their noble galvanic properties. Several standards directly advise against using such gaskets for seawater systems. The performed tests partly support this view, but do not clearly demonstrate the detrimental effect of graphite because the spiral was made from a stainless steel grade having a lower corrosion resistance than the flange face.

Other parameters and aspects affecting crevice corrosion have been discussed as well, such as flange tightening, gasket setting and preventive measures.

6 References

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