

Crevice Corrosion of High-Grade Stainless Steels in Seawater: A Comparison Between Temperate and Tropical Locations

Nicolas Larché
French Corrosion Institute, RISE
220 Rue Rivoalon
29200 Brest
France

Charles Leballeur
French Corrosion Institute, RISE
220 Rue Rivoalon
29200 Brest
France

Dominique Thierry
RISE KIMAB
Isafjordsgatan 28A
164 40 Kista,
Sweden

Erwan Diler
French Corrosion Institute, RISE
220 Rue Rivoalon
29200 Brest
France

ABSTRACT

The corrosion risk for stainless steel components is not the same in all seawaters, with more failures generally reported in tropical seas. In this study, the influence of biofilm on electrochemical behavior and corrosion resistance of passive films of high-grade alloys was studied in different seawaters, including temperate seawater (France-Brest, North Atlantic Ocean), tropical seawater (Malaysia-Kelatan, Meridional China Sea), and intermediate conditions in terms of temperature (Brazil-Arraial do Cabo, South Atlantic Ocean). The stabilized open-circuit potentials and the polarization behavior of high-grade stainless steels were measured as function of temperature in all the tested field marine stations, providing quantified data and direct comparison on the biofilm-enhanced corrosion risks. Significant differences were measured in tropical and in temperate seawaters in heated conditions above 30°C. In parallel to the monitoring of biofilm-induced depolarization, crevice corrosion of 8 high grades passive alloys was studied with the use of crevice formers specifically developed for tube geometries. Duplex, superduplex, hyperduplex and 6Mo stainless steels tubes have been evaluated together with Ni-based alloys. The corrosion results are discussed regarding the monitored biofilm-induced depolarization measured in the different test conditions.

Key words: Crevice corrosion, Seawater, Biofilm, Ennoblement, CRA's, Stainless steels.

INTRODUCTION

In natural seawater, microorganisms can fix, grow and develop on practically any surface, including stainless steels [1–3]. The term biofilm is generally used for communities of microorganisms embedded in an organic polymer matrix (e.g. exopolysaccharides), produced by the microorganisms themselves)

and adhering to a surface, irrespective of the environment in which they develop. [4]. Stainless steels are widely used for different applications in seawater such as the oil and gas, desalination and marine energy industries. The presence of a biofilm on passive alloys such as stainless steels or nickel-based alloys can strongly enhance the cathodic reactions, [5] and shift their open-circuit potential (OCP) to the noble direction [6,7]. The resulting increase in OCP is also called cathodic depolarization or ennoblement. The ennoblement in aerated seawater is known to be one of the main factors affecting the risk of localized corrosion of stainless steel and nickel-based alloys, since their critical pitting or crevice potential for protective passive layer breakdown can be exceeded [8]. Among the mechanisms that could explain the so-called ennoblement, some authors mention the role of microbial enzymes, the production of H_2O_2 , and/or low pH inside the biofilm or at the biofilm/stainless steel interface [9–12]. Some recent studies also suggest the role of electroactive bacteria [13,14]. Cathodic depolarization also called electroactive biofilms has been observed in different seas around the world, [7,15–22] including in deep sea [23]–[24].

Biofilm monitoring systems using different techniques exist and are well described in the literature which details the different possible approaches [22,25]. Among these techniques, the method based on biofilm catalysis of oxygen reduction measures the degree of cathodic depolarization of stainless steel induced by the formation of a biofilm [26–28]. The electrochemical activity of natural aquatic biofilms was proven to be proportional to the surface area covered by bacteria [29–31]. This phenomenon allows the quantification of electroactive biofilms and makes possible the assessment of the associated corrosion risks. The sensing methods are based on either the potential ennoblement time and/or the cathodic current monitoring. Thus, these monitoring methods rely on measurements of the current between a passive and a more anodic material through a shunt resistor, or at fixed potential by the use of a potentiostat [29–31]. Potentiostatic polarization proved to provide detailed information on the rate of biofilm development from less than 1% up to a complete coverage of the surface [32–34]. The use of several applied potentials allows drawing pseudo-polarization curves. The term “pseudo”-polarization curves means that several coupons (tested at different potentials) are used to build the complete curve, allowing to draw long-term and realistic polarization behavior. The increase of the biofilm-enhanced current on stainless steel was well described by Mollica and Scotto, and is well illustrated in Figure 1, showing that polarization behavior of stainless steel is significantly evolving with the biofilm formation [35]. In this figure, 6 samples (*i.e.* 6 applied potentials) are used to draw the pseudo-polarization curve that evolves with time (*i.e.* with the biofilm settlement).

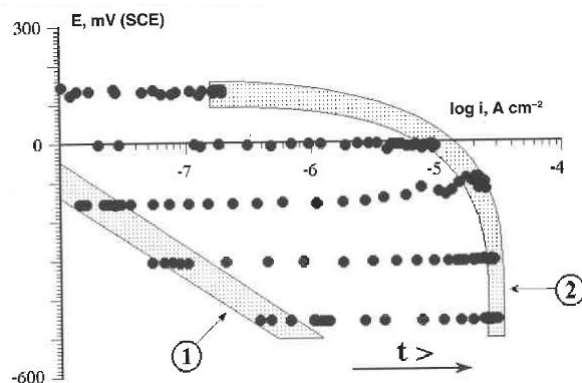


Figure 1: Illustration of the biofilm-induced cathodic current increase obtained from potentiostatic exposures of stainless steel in natural seawater. 1- pseudo-polarization before biofilm formation, 2- pseudo-polarization after biofilm formation [35]

However, a possible drawback of such a setup is that under polarization the surface pH increases and associated species precipitation occurs, such as $CaCO_3$ and $Mg(OH)_2$, changing the expected service conditions [36]. Thus, the biofilm growth and activity depend upon the experimental setup which shall be carefully considered in the analysis of the data.

The biofilm-induced cathodic depolarization is known to be temperature dependent. For instance, no ennoblement has been reported in the North Sea at temperature above 32°C, whereas a temperature limit of about 37°C has been reported in the bay of Brest (North Atlantic Ocean), in where no ennoblement was observed after several months of exposure [7,19,37]. In addition the kinetic of ennoblement is temperature dependent with higher incubation time at low temperatures [38]. In a recent project, the potential ennoblement has been measured in tropical seawaters including Singapore, Saudia, Caribbean Sea and Brazil. [21] From these results, it was shown that (a) potential ennoblement occurred for all tested seawaters with rather similar results for all sites at 30°C, and (b) no ennoblement was observed in Brest (temperate seawater) above 37°C after 3 months of exposure while biofilm ennoblement was still measured at 45°C in Singapore. From the results of this study, the temperature and its effect on ennoblement were confirmed to be a major parameter to assess the localized corrosion of passive alloys since above 37°C large differences were highlighted in terms of potential ennoblement between temperate and tropical seawaters. Such temperatures can be easily reached in Oil & Gas offshore, desalination and marine energy systems, where heat is produced. Thus, there is an interest to quantify the localized corrosion resistance of materials in heated tropical seawaters as data obtained in temperate seawater may not be representative. Indeed, in tropical seas above 40°C, ennoblement may still be present and consequently the corrosivity is expected to be higher. However, the safe maximum temperature will also largely depend on the severity of the crevice geometry[39]. In the present study, electroactive biofilms and associated corrosion risks were investigated in different seawaters (tropical and temperate) and at different temperatures. The effect of crevice geometry was also studied.

EXPERIMENTAL PROCEDURE

Materials

The alloys, product forms, and geometries of the tested samples are given in Table 1. The chemical compositions are given in Table 2 together with their pitting resistant equivalent numbers (PRENw). For all materials, tube/bar geometry has been tested. Hot rolled plates made of superduplex UNS S32750 have been used for biofilm monitoring (cf. biofilm module). For corrosion exposure, UNS S39274, S32707, S33207, N06845, N06625 and S33205 seamless tubes were tested, while UNS S31266 was tested as bar product. For the superduplex UNS S32750, rolled-welded tubes have also been tested. The duplex UNS S32205 was tested as low resistant reference for seawater applications. The nickel-based alloys UNS N06625 and N06845 were tested for comparison purpose with the stainless steel materials.

Table 1: Tested materials, product forms and geometries

ALLOY UNS.	PRODUCT FORM	GEOMETRY
S31266	Bar	OD = 36 x L=100 mm
S32750	HR (Hot Rolled) Plates	150 x 100 x 6 mm
	Seamless tubes	OD22,83 x WT1,89 x L=150 mm
	Rolled-Welded (RW) tubes	ID19,05 x WT1,06 x L=150 mm
S39274	Seamless tubes	OD23,09 X WT2,02 x L =150 mm
S32707	Seamless tubes	OD25,4 x WT1,65 x L=150 mm
S33207	Seamless tubes	OD26,29 x WT3,62 x L=150 mm
N06845	Seamless tubes	OD23,09 X W 2,02 x L =150 mm
N06625	Seamless tubes	OD31,0 x WT2,8 x L=150 mm
S32205	Seamless tubes	OD25,4 x WT1,95 x L=150 mm

OD = Outer Diameter, ID = Inner Diameter, WT = Wall Thickness, L=Length

Table 2: Chemical composition of tested alloys (%wt).

ALLOY UNS.	PRODUCT FORM	Si	Mn	Cr	Ni	Mo	N	Co	Nb	W	Ti	Al	Fe	Cu	PREN _w *
S31266	Bar	0.20	2.50	24.1	22.0	5.50	0.50	-	-	2.01	-	-	bal	1.70	54
S32750	HR plate	0.25	0.70	25.1	7.0	3.8	0.29	-	-	-	-	-	bal.	0.20	42
	Seamless tubes	0.31	0.37	25.3	6.4	3.9	0.30	-	-	-	-	-	bal.		43
	Rolled-Welded (RW) Tube	0.32	0.76	25.5	6.9	3.9	0.30	0.16	-	0.09	-	-	bal	0.24	43
S39274	Seamless tubes	0.32	0.43	24.7	6.7	3.2	0.28			2.12			bal.	0.47	43
S32707	Seamless tubes	0.27	1.02	26.9	6.4	4.8	0.38	1.00	-	-	-	-	bal.	-	49
S33207	Seamless tubes	0.21	0.95	31.5	7.3	3.4	0.48	-	-	-	-	-	bal.	-	50
N06845	Seamless tubes	0.20	0.20	23.1	45.8	6.2	-	-	-	4.00	-	-	bal.	2.80	50
N06625	Seamless tubes	0.22	0.17	22.8	58.2	9.0	-	0.15	3.60	0.38	0.38	0.24	4.71	-	53
S32205	Seamless tubes	0.56	0.76	22.3	5.2	3.1	0.17	-	-	-	-	-	bal.	-	35

*Pitting Resistant Equivalent Number_w = %Cr + 3.3 (%Mo + 0.5%W) + 16%N

Metallographic inspections of tested alloys were performed. For all these materials, the expected microstructure was observed (*i.e.* expected ferrite/austenite balance of 50/50 for duplex and superduplexes) without defects.

The roughness of test specimens (tubes, bars and plates) was quantified with 3D-Optical profiler system, using interferometry technique. For all tested tubes (seamless and rolled-welded) and rods, the roughness was similar with $R_a = 0.3 \pm 0.05 \mu\text{m}$ (measured on 10 replicates per tested alloy). The roughness of all as-received tested plates was $2.2 \pm 0.5 \mu\text{m}$.

Characterization of the biofilm ennoblement

One of the main objectives of the study was to define for each test site (*cf.* tropical and temperate seawaters) the maximum temperature for which biofilm-enhanced ennoblement on stainless steel is still observed. For this purpose, the OCP of superduplex stainless steel tubes (S32750) were measured at increasing temperatures from the ambient and until ennoblement is not detected anymore (*i.e.* no ennoblement measured after 2 weeks for each tested temperature). The exposures were performed in non-metallic exposure tanks of about 300L containing continuously renewed seawater at a rate of about 300L/day (*i.e.* one complete volume of the tank per day), and equipped for temperature regulation with an accuracy of $\pm 1^\circ\text{C}$. For all systems, regulated Teflon-coated thermo-heater have been used together with a continuous stirring (pumps), ensuring a homogenous environment in the exposure tanks. The potentials were measured with AgAgCl/KCl-gel electrodes, calibrated with a saturated calomel electrode (SCE). All results are reported versus the SCE scale. The potentials were recorded using high impedance ($>10^{11}\Omega$) data loggers, adapted for electrochemical measurements.

Biofilm-ennoblement was also characterized with cathodic current and corrosion potential measurements of superduplex stainless steel UNS S32750. For this purpose, 6 superduplex stainless steel plates (150 x 100 cm) were connected to a zinc anode through different resistors designed to provide potential range from OCP to approximately -700 mV/SCE. This method is detailed elsewhere [23]. In such system (referred as “biofilm module” in this paper), the biofilm-induced depolarization is followed by an increase of the cathodic current. As mentioned in the introduction, this technique appears very interesting to characterize the electrochemical effect of biofilms and to assess at the same time the corrosion risk (regarding the existing correlation between cathodic efficiency and localized corrosion rate). The biofilm modules have been deployed in France (Brest, Atlantic Ocean) and in Malaysia (Kelatan/Bachok, Tropical China Meridional Sea).

Crevice corrosion tests

The objective was to assess the crevice corrosion susceptibility of different stainless steel grades and nickel-based alloys in simulated and natural tropical seawaters. For this purpose, the crevice assembly defined in ISO18070:2015⁽¹⁾, generally used for plate geometries, was adapted [40]. This standard assembly allows a rather good control of the pressure at the gasket location. The crevice assembly has the following characteristics: crevice formers are made of polyvinylidene fluoride (PVDF), all fasteners are made of titanium grade 2 and are electrically isolated from the tested specimen. Disc springs can be used to keep a measurable and constant pressure between the crevice formers and the specimen. According to this standard, the crevice former should be tightened to the test specimens with a force of about 900N (*i.e.* pressure of about 3 N/mm²), which corresponds to a torque of 3 N.m on the used fasteners. All electrical connections used for the monitoring of the open-circuit potential of the specimens are made of titanium grade 2. The anode (surface under crevice formers) to cathode (surface in contact with seawater) ratio was about 1:30. The standard parameters of the ISO18070:2015⁽¹⁾ were modified in order to increase the severity of the crevice geometry and reach a higher pressure of about 20 N/mm² at the gasket location, which is considered as a more severe configuration, more representative of industrial applications such as threaded connection or flanges [39,41]. For tube and bare geometries, an adapted crevice former was used, allowing the use of both gasket pressures of 3 and/or 20 N/mm², on gasket surface equivalent to ISO18070:2015⁽¹⁾ crevice former used for plane surface [42]. A schematic drawing and a photograph of this last assembly is given in Figure 2.

⁽¹⁾ ISO 18070:2015 - Corrosion of metals and alloys -- Crevice corrosion formers with disc springs for flat specimens or tubes made from stainless steel

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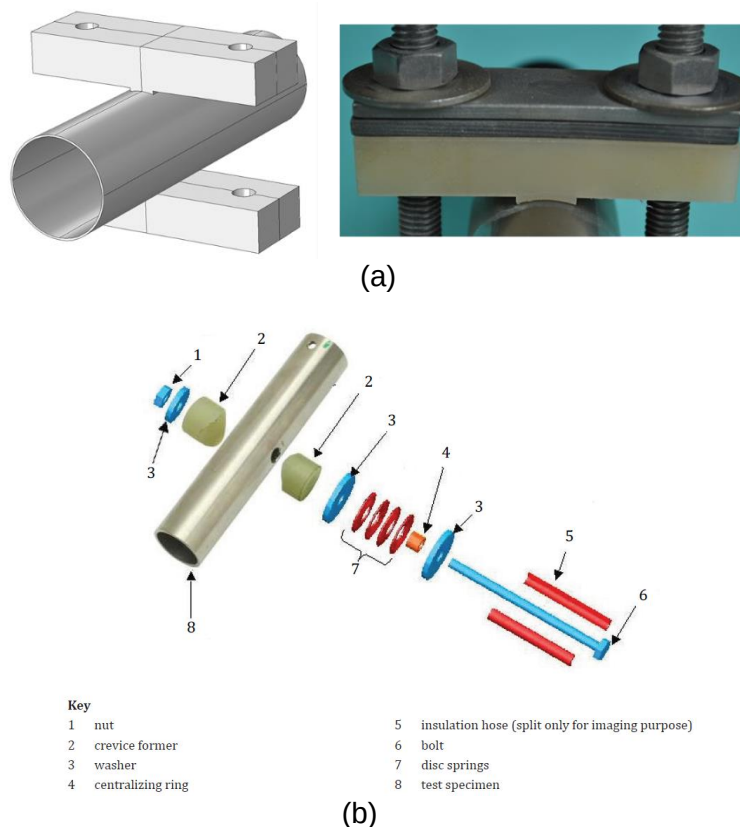


Figure 2: (a) Schematic drawing and photograph of the adapted crevice former for tube or bar geometries, allowing gasket pressure of 20 N/mm² and (b) standard crevice former from ISO18070:2015

The advantages of the above crevice assemblies on tube geometries are (a) it allows a direct comparison with plate geometries tested with ISO18070:2015 since similar surface areas and gasket pressures are involved, (b) the actual surface roughness of produced tubes or bars can be evaluated, (c) it allows high gasket pressures (20 N/mm²), representative of possible cases in the industry (e.g. pressure at sealing elements...), (d) no tube drilling is required (that could influence local geometry and local pressure), and (e) it allows an homogeneous/controlled repartition of the pressure below gasket. This was confirmed by Finite Element Modelling [42]. For each tested configuration (tube, bare, plate), 6 replicates were used. It is important to mention that for rolled welded specimens, one of the two crevice gaskets was placed on the longitudinal weld to determine if this is a preferential corrosion area.

After exposure, a complete evaluation of the corrosion was performed for each tested specimen including visual evaluations, binocular and microscopic evaluations of the corrosion using optical microscopy (corroded area, maximum corrosion attacks evaluated with optical focalization connected to micrometric gauge). Metallographic inspections were also performed on selected samples at corroded areas

Exposure sites and test conditions

The biofilm ennoblement and corrosion investigations were conducted at 3 selected locations, covering different kind of seawaters in terms of temperature levels and seasonal variations. The main characteristics of the test sites were measured during the year of exposure (Table 3). France (Brest) and Brazil (Arraial do Cabo) sites are facing season-induced change of temperature while the Malaysian site (Kelantan/Bachok), close to the equatorial line, have almost constant temperature during the whole year (around 30°C). Mean salinities ranged from 31 to 36 ‰, with the lower value for Malaysian site. The mean pH was quite similar from 8.1 to 8.3. The dissolved oxygen contents are in good line with saturation values at mean temperatures (*i.e.* DO around 8 ppm at 12°C and 6 ppm at 30°C).