

Behaviour of stainless steel in natural seawater

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ABSTRACT

In this paper, investigations performed in natural and artificial seawater on stainless steels will be presented. They concerned studies on: biofilm formation, passive layers composition, electrochemical behaviour, localised corrosion and the evolution of these different parameters as a function of ageing time. According to literature surveys, the different aspects will be discussed. Some conclusions will be drawn concerning the actual knowledge on the behaviour of stainless steels in seawater.

INTRODUCTION

The behaviour of stainless steels in natural seawater is of great interest since they are widely used in marine structures. Stainless steels such as 316L, 304..., present a poor corrosion resistance in seawater. Their durability is altered by the corrosive nature of the marine environment. It is well-known that exposure of stainless steels, as well as any kind of materials in natural seawater induces the development of a microbial film, the biofilm. Many investigators have focused their attention on the interactions between fouling and electrochemical corrosion. Recent reviews on this subject are reported in the literature¹⁻³.

In this paper, studies performed in natural and artificial seawater by IFREMER will be presented, they concerned studies on: biofilm formation, passive layers composition, electrochemical behaviour, localised corrosion. The different aspects will be discussed according to literature surveys.

BIOFILM SETTLEMENT ON STAINLESS STEEL

Numerous laboratory studies as well as real-life experiments on materials immersed in seawater highlighted different stages in the formation of biofilm.

The first step, occurring within minutes of exposure, corresponds to the adsorption of organic macro-molecules (exopolymers, glycoproteins, humic acids) and/or inorganic macro-molecules already present in the environment or produced by the micro-organisms⁴⁻⁵. This conditioning film is essential because the induced modifications of the surface properties (surface tension, surface energy⁶⁻⁷, polarity, mouillability) will permit a subsequent adhesion of bacteria.

The bacterial adhesion itself occurs in a two-stage process, few hours after immersion⁸⁻¹⁰. The bacterial attachment to the substrate is first reversible but becomes irreversible due to the secretion of extracellular polymers (acid exopolysaccharides), developing polymeric bridging between the cell and the substrate.

Once film attachment has occurred and if the physico-chemical conditions at the interface are adequate, bacteria grow on the surface as micro-colonies. These colonies and their extracellular secretions form the biofilm.

The bacteria adhesion, the biofilm formation and its growth depend on different factors as the environment physico-chemical properties (temperature, salinity, dissolved oxygen, organic matter content, etc.), the substratum nature and micro roughness, the hydrodynamic conditions at the surface¹¹.

Figure 1 shows biofilm growth on stainless steel (SS) from 2 to 21 days of immersion in natural seawater during spring.



Figure 1a

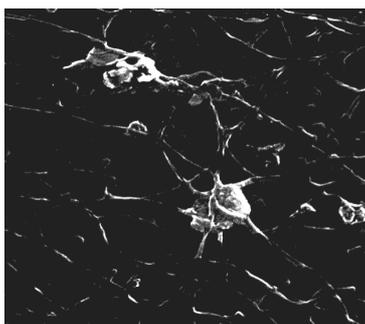


Figure 1b



Figure 1c

Figure 1 : Evolution of biofilm on 316L SS surface after 2 days (1a), 9 days (1b) and 21 days (1c) in natural seawater (magnification 2000)

EVOLUTION OF THE PASSIVE FILMS

A lot of studies have been performed on passive films behaviour of SS in aqueous solutions containing chloride^{12,13} or neutral free chloride solutions¹⁴, but it seems to have a lack of information on the evolution of passive films during normal use. The effect of ageing in natural¹⁵ and artificial seawater¹⁶⁻¹⁷ on the composition and thickness of passive films has been evaluated using X-ray Photoelectron Spectroscopy (XPS) and Auger Spectroscopy (AES). Indeed, the composition of the oxide film of course depends on the chemical composition of the alloy and on the surface preparation.

In the case of Fe20Cr alloy¹⁸, a thin Cr-enriched oxide film covered the surface after electropolishing and cathodic reduction in a borate buffer solution (pH 8,4). Costa and co-workers¹⁵ showed that the initial layer covering the surface of 316L SS after polishing and rinsing in ethanol, was composed of an homogeneous film (50% Fe oxides and 50% Cr oxides) with an average thickness of 25-30 Å. After a chemical treatment with HF and HNO₃ followed by a repassivation with HNO₃, the oxide film on 316L SS is an homogeneous film composed of 20% Fe oxides and 80% Cr oxides and hydroxides. The initial passive layers were around 20 Å thick. As a function of ageing, from 2 to 21 days in natural seawater, thickness passive films keep a constant value of 30-40 Å. However, a stratification in the oxides layers structure was detected with exposure time. It consisted in an enrichment of Cr hydroxides in the inner part of the film and a depletion of Cr oxides. Rondot and co-workers¹⁶⁻¹⁷ showed that the Cr hydroxides content also increased in 316L SS chemically treated as above (in HF and HNO₃) but aged in artificial seawater. AES analyses of 316L and URANUS SB8 revealed a thin film mainly composed of Cr₂O₃ in the inner layer whereas the external region was deficient in chromium and rich in iron. These results agree with those obtained by Ramasubramanian et al.¹⁹ who noticed that films formed on 316L SS in borate-boric acid buffer (pH 8.6) at potentials over 0V/SCE consisted of at least two parts: outer layers of mainly ferric oxides and inner layers rich in chromium species. At potentials under 0V/SCE, chromium oxides mainly constituted the passive layer.

Modifications in the passive film could be explained on the basis of selective solubility of the oxides at the applied potentials or at potentials reached after ageing in seawater.

ELECTROCHEMICAL BEHAVIOUR OF STAINLESS STEEL

Ennoblement of free corrosion potential

Artificial seawater

An increase in the free corrosion potential (E_{corr}) of SS is observed with immersion time in artificial seawater. Johnsen and Bardal²⁰ showed that a stable potential of approximately +100mV/SCE was reached on SAF 2205 SS after 8 days in artificial seawater. Similar results were obtained by Scotto and co-workers²¹ on various stainless steels exposed in artificial seawater sterilised in autoclave or by filtering (0.22 µm). The sterilisation eliminates not only microbic and micro-alga components but also high molecular weight organic substances easily adsorbed by metal substrata.

Figure 2 shows the evolution of the free corrosion potential of 316L and URANUS B8 SS in artificial seawater¹⁷. At the beginning of immersion, the potential rapidly decreases down to -300 mV/SCE then rises up to around 0 mV/SCE. The artificial seawater was not sterilised and allowed the development of micro-organisms but the biological activity found in these conditions was far from that found in natural seawater. This increase in free corrosion potential may be explained by an evolution of

the chemical composition of the passive film. From capacitance measurements, Rondot and co-workers¹⁶⁻¹⁷ highlighted a decrease in the doping density of the passive film as a function of immersion time which was responsible for the rise of corrosion potential.

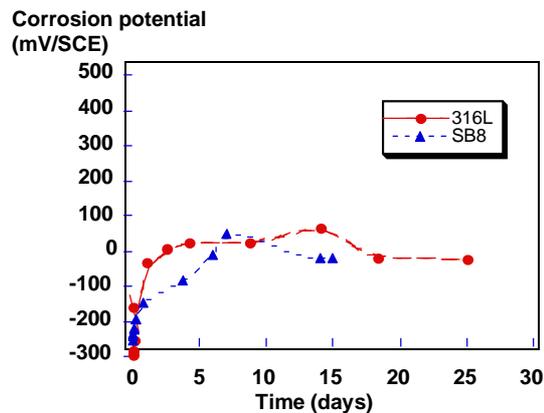


Figure 2: Evolution of the corrosion potential of 316L and S08932 (URANUS B8) plates during immersion in artificial seawater.

On the contrary, Dupont²² did not observe any ennoblement of SS corrosion potential in experiments conducted in artificial seawater sterilised in autoclave. Steady values of -180 mV/SCE were measured during the exposure time (8 days).

The relatively low microbial activity in artificial seawater depending on the sterilisation techniques seems to limit or sometimes to inhibit the corrosion potential increase.

Natural seawater

It is now admitted that a free corrosion potential ennoblement of SS appears after immersion in natural seawater.

This was clearly demonstrated in the European collaborative project : "Marine biofilm on stainless steel - effects, monitoring and prevention", partially funded by the European Communities in the framework of the Marine Science and Technology program and by the Round Robin Tests performed by the EFC Working Party on Marine Corrosion²³⁻²⁷. An ennoblement of E_{corr} was observed in all cases^{20-21,23-30}, independent of the exposure geographical location or season, and of the composition (nickel, chromium or molybdenum content) and microstructure of SS.

Some discrepancies occurred between the effects of seasonal variations on the free corrosion potential increase. The evolution of E_{corr} was related to the seasonal exposure and was greatly influenced by the seawater temperature among other parameters. Indeed, it has been shown^{22,28,31} that the ennoblement could be prevented by sufficiently increasing seawater temperature (up to around 40°C). Examination of the Electron Transport System (ETS) activity and the Adenosine TriPhosphate (ATP) content showed that rising the temperature to 40°C caused a diminution in biological activity but certainly not the disappearance of all viability. This would suggest that heating seawater to 40°C may be sufficient to inhibit bacteria activity. Mollica and co-workers³¹ also observed that a temperature rise to 40°C had the same effect as mechanical cleaning or addition of biocides. Indeed, the elimination of living bacteria by addition of biocides (NaN_3) which acts as respiratory inhibitor, prevented the potential increase²¹⁻²². However, attention must be paid to the effect of temperature on the oxygen solubility in seawater : increasing temperatures induces a diminution in oxygen solubility. From the Mast project²³⁻²⁶, the increasing rate was slower in winter than in summer or autumn and the incubation time prior to the

potential increase was the shortest when the seawater temperature was the highest, i.e. generally in summer (Figures 3a and 3b). From the EFC project²⁷, opposite results were observed, the potential increase was lower during summer than winter. The final value of E_{corr} was rather similar in all cases, around 300 to 350 mV/SCE, independent of the hydrological conditions or sites except those from a few laboratories²⁷ which have recorded higher potentials (over 450-500 mV/SCE) and lower potentials in Antarctica seawaters³² (never overcoming 50-100 mV/SCE). However, this final value depended on the flow rate conditions. Experiments investigated in our laboratory³⁰ showed that the final values were slightly higher in laminar than in turbulent flow. A difference of around 50 mV was measured. The incubation time i.e. the delay before reaching a steady potential was also a function of hydrodynamic conditions: this parameter was approximately as twice important in turbulent case as in laminar case. Mollica and Trevis³³ showed that the delay time was increased and the degree of ennoblement decreased by increasing the flow speed of seawater. The same observations were obtained in the MAST project²³⁻²⁶, the potential ennoblement was always faster on plates (exposed in almost stagnant seawater) than on tubes (with seawater flow rates from 0.1 to 1.0 m/s according to Partners utilities) with a shorter incubation time and a faster increasing rate. Thus, increasing the flow rate seems to retard the formation of the microbial film. Considering the effects of hydrodynamic conditions²⁸, a critical rate for the settlement of a microbial film was found at about 2m/s. According to Johnsen and Bardal²⁰, the potential was less influenced by the seawater velocity.

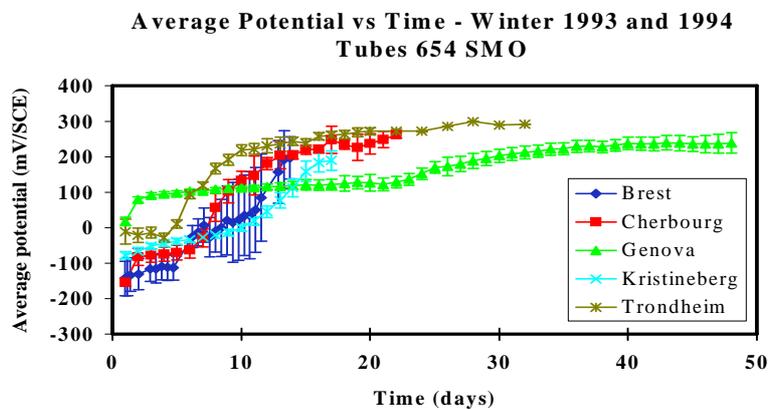


Figure 3a

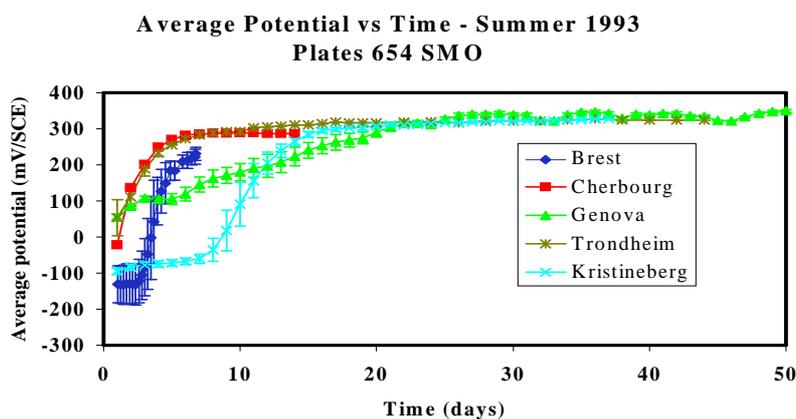


Figure 3b

Figure 3 : Evolution of the open-circuit potential exhibited by 32654 (654 SMO) tubes and plates at the five marine stations 3a: during the winter exposure period, 3b: during the summer exposure

period. The results correspond to a mean value obtained on 5 to 20 specimens \pm the standard deviation. Results of the MAST project ²³⁻²⁶.

No evident correlation²³⁻²⁶ was noticed between the free corrosion potential evolution and the hydrological parameters (chlorophyll A, pH, salinity, ash content, organic matter content...).

The effects of sunlight on ennoblement of E_{corr} is of great interest. Much industrial uses of SS alloys are for tanks, piping and heat exchanger tubing, where the immersed portion of the structure is in the dark. However, data on the effect of light on E_{corr} are rather conflicting. Dexter and Zhang³⁴ showed that, in all waters under low light conditions, the level of ennoblement was usually 100 to 200 mV higher than in the daylight. It is thought that the action of photosynthetic algae and bacteria, which can change the pH, O_2 and CO_2 concentrations within the biofilm, would be responsible for such difference. According to Motoda et al.²⁹, the corrosion potential under darkness reached values 100 mV higher and increased much slower than under light exposition. However, no effect of sunlight shielding was found after 20 days of immersion. Eashwar and co-workers³⁵ noticed a similar behaviour of corrosion potential as a function of light level. Little et al.³⁶ observed an evolution of E_{corr} toward more negative values for SS immersed in the Gulf of Mexico under dark conditions, whereas ennoblement occurred in the sterile solution. The presence of sulphate-reducing bacteria (SRB) seemed to be responsible for this behaviour according to results obtained by Ringas et al.³⁷ with SS in cultures of SRB; they found a similar decrease in E_{corr} . Based on Mansfeld et al.³⁸ results, no significant effects of light or darkness conditions were observed. Ennoblement were measured when biofilms developed under fully illuminated conditions³⁶ where the interface remained aerobic.

This leads to the conclusion that the corrosion potential evolution as a function of immersion time, is strongly affected by the presence or the absence of microbial activity in the test environment. Since the biofilm growth seems to have an important role in the ennoblement, the free corrosion potential increase is clearly higher in natural seawater than in artificial seawater, the effects of composition, thickness and ageing of passive films in seawater must not be neglected.

Oxygen reduction reaction modifications

The potential increase in the presence of a biofilm in seawater environment has been observed on various stainless steels. According to Varjonen³⁹, the fact that specimens have the same passive current both in natural and artificial seawater leads to the conclusion that the ennoblement is certainly accompanied by a modification of the cathodic reaction. For this reason, studies on the evolution of the cathodic reactions are of great interest.

The cathodic processes include oxygen reduction reaction and hydrogen evolution. In the corrosion mechanisms, the oxygen reduction is often described as following a 4 electrons transfer⁴⁰. However, hydrogen peroxide can often be formed as an intermediate or as a final product of oxygen reduction⁴⁰. Few studies have been performed on various environments, various metals (Gold, Platinum, Copper, Iron...) ⁴¹⁻⁴³ and alloys such as stainless steels⁴⁴⁻⁴⁶. A general agreement seems to be reached on the importance of the material balance, the nature of the surface oxide present (oxidation degree, electronic properties...), the existence of one or more limiting currents. Until now, only a few investigations on the evolution of the oxygen reduction with ageing time have been performed. Scotto and co-workers⁴⁷ observed modifications on the cathodic kinetics. A shift of the cathodic curve to higher currents and potentials appeared as a function of immersion time in natural seawater. The cathodic reaction became diffusion controlled. Such modifications have also been observed in our laboratory. Figure 4 shows the evolution of the oxygen reduction reaction⁴⁸ at a rotating disk electrode (RDE) of SS at different exposure times. Changes in the curve shape occur immediately after immersion within a few

hours. This first evolution should be attributed rather to a modification in the passive layer than in the effect of a microbial film. After longer immersion time (over 1 month), stable oxygen reduction curves are registered. Johnsen and Bardal²⁰ showed the effects on the current density for cathodically protected stainless steels. The applied current necessary to hold the sample at a potential of -400 mV/SCE increased as a function of biofilm establishment, and as the biofilm became in equilibrium at the interface, a decrease of the current was observed. Similar conclusions on the evolution of current applied for cathodically protected stainless steels with time have been brought by other investigators^{28-29,31,49-50}. Experiments carried out at higher temperature (40°C) by Mollica et al.³¹ showed no evolution in the oxygen reduction kinetics with time and no difference with curves obtained in sterile environment. This result leads to the conclusion that the bacterial settlement in the temperature range <35°C would modify the oxygen reduction.

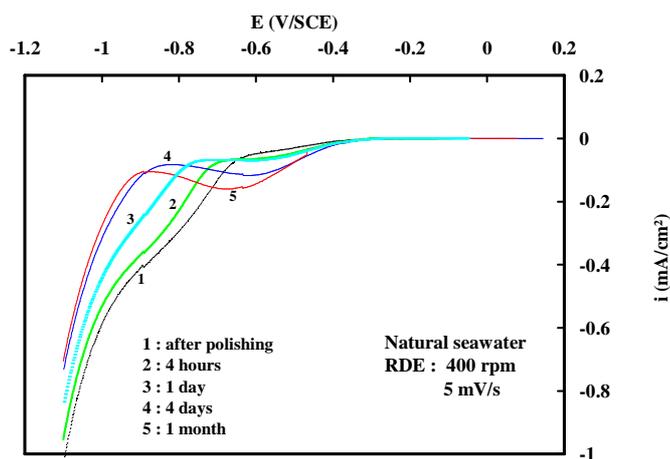


Figure 4 : Cathodic polarisation curves on Rotating Disk Electrode (RDE) of S08904 (URANUS B6) SS as a function of immersion time

The mechanisms of these effects are not completely understood. However, hypothesis have been proposed to explain the ennoblement of the free corrosion potential and the reasons for the modifications in cathodic activity.

The general ennoblement of the free corrosion potential could be explain by the mixed potential theory³ where changes in electrochemical parameters would be involved as follows⁴⁹ :

- increase of the reversible potential of oxygen,
- increase of the exchange current density of the oxygen electrode,
- decrease in the cathodic Tafel slope,
- decrease in the passive current density.

The last hypothesis seems to be excluded as Scotto⁴⁷ found that the passive current was not changed by biofilm growth. An increase in the reversible potential of oxygen is unlikely since the presence of a bacterial film decreases the O₂ concentration by acting as an oxygen diffusion barrier or/and by consuming the O₂ in their metabolism⁴⁹.

Considering the enhancement of cathodic activity by biofilm, several explanations have been proposed. First, a catalytic effect by organometallic complexes could be involved⁴⁹. It is known that the adhesion of bacteria to the surface occurs by producing an extracellular polymer, generally an

extracellular polysaccharide called EPS. These EPS are able to bind metallic ions such as Cu^{2+} , Fe^{2+} ... which can serve as oxygen reduction catalysts⁵¹. Catalytic effects by porphyrin-type organo-heavy metal complexes or enzymes from the respiratory system of the organisms forming the biofilm could also be involved in the processes of O_2 reduction⁵². Polypyrroles are semi-conductors which can incorporate metal complexes and which present high catalytic activities in oxygen reduction⁵³. However, no evidence of the presence of polypyrroles in biofilm has yet been performed, but, this hypothesis can not be excluded. Secondly, bacterially produced enzymes could enhance cathodic processes^{21,31}. Indeed, bioelectro-catalytic mechanisms can accelerate the rate of electrochemical reactions by some enzymes with oxidase activity, whereas the electron transfer from the metallic surface to the enzyme can be carried by means of mediators⁵⁴ (polypeptides⁵⁵, proteins⁵⁶). The respiratory enzyme system of aerobic organisms is hypothesised to produce hydrogen peroxide which is supposed to accelerate the oxygen reduction^{22,57}. Dupont²² has detected H_2O_2 as the by-product of glucose oxydase enzyme activity. A correlation between the ennoblement of E_{corr} and H_2O_2 production combined with acidic pH has then been observed. However, a precision must be brought on the fact that H_2O_2 could also be produced by electrochemical reduction of O_2 . Moreover, H_2O_2 has a bactericidal action which could induce a diminution of bacterial population on the surface⁵⁸. Salvago et al.² showed that acidic environment formed at the interface surface/biofilm leads to modifications of the cathodic reaction by altering the passive layer. Among the proposed mechanisms, some authors have suggested that the ennoblement of E_{corr} would be caused not by the metabolism but by the metabolite of the sea diatoms included in the organic film²⁹. The electronic nature of the passive films has also probably a strong effect on the reduction of O_2 ⁴⁴.

Based on the different hypothesis, it seems unlikely that a sole explanation would be sufficient to explain the ennoblement of E_{corr} . A combination of different mechanisms is probably involved in the electrochemical behaviour of stainless steels. Ongoing researches will bring more information on the subject.

Although the mechanisms of the biofilm effects are not completely understood, the consequences on stainless steels can be predicted from the mixed potential theory. The free corrosion potential increases near the breakdown potential values and enhances the probability of pitting corrosion. However, the pitting potential also changes as a function of ageing time.

LOCALISED CORROSION

Stainless steels exposed to seawater may suffer from localised corrosion such as pitting, crevice and stress corrosion cracking.

Pitting corrosion

Localised corrosion is governed by random parameters and analysed according to the stochastic theory. Therefore, the distribution of the breakdown potentials on 316L was analysed at IFREMER as a function of ageing time in seawater and of the open-circuit potential values⁵⁹⁻⁶⁰. The importance of these two parameters on the elementary pitting probability per unit area (ω), determined under potentiokinetic conditions, was also evaluated from a statistical point of view.

The pitting potential⁶⁰ also changes with ageing time and the evolution of the mean open circuit potential and of the pitting potential are given as a function of time in Figure 5. Since the standard deviation evolution of these two parameters indicates a wide scattering of the results, a stochastic approach to pit initiation was preferred. From Zhang and Dexter⁶¹, biofilms increase the critical pitting corrosion of 304

SS but no differences were observed for 316 SS. However, the number of samples was limited; in Figure 6, a minimum of 50 samples was used for each exposure time.

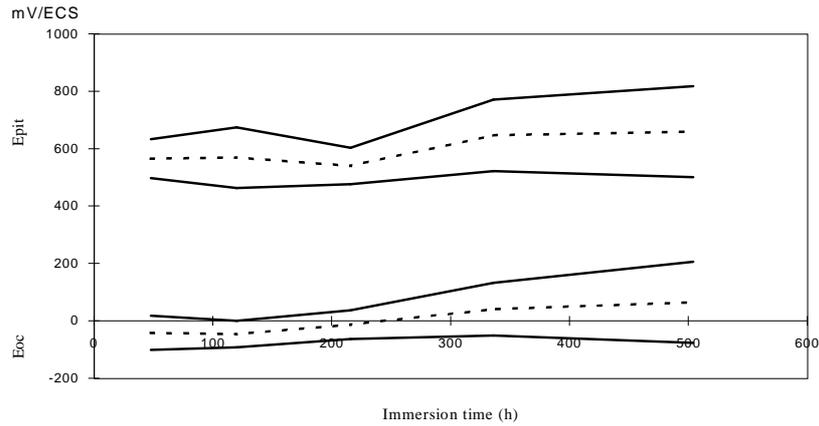


Figure 5: Evolution of the mean value of open circuit potential and pitting potential as a function of time.

A peak in distribution is observed after 2, 5, and 9 days of immersion around 515 mV/SCE, Figure 6. After 14 and 21 days of immersion, no peak is observed anymore since the pitted samples are evenly distributed over the whole potential range. Another peak is observed for long periods of immersion, over 60 days, in natural seawater at very high potential values around 1100 mV/SCE. After a long immersion time, a competition phenomenon appears between pit generation and secondary passivation depending on the scanning rate. These results explain the extremely high values of breakdown potentials, around 1100 mV/SCE, for long immersion time and for high value of open-circuit potential.

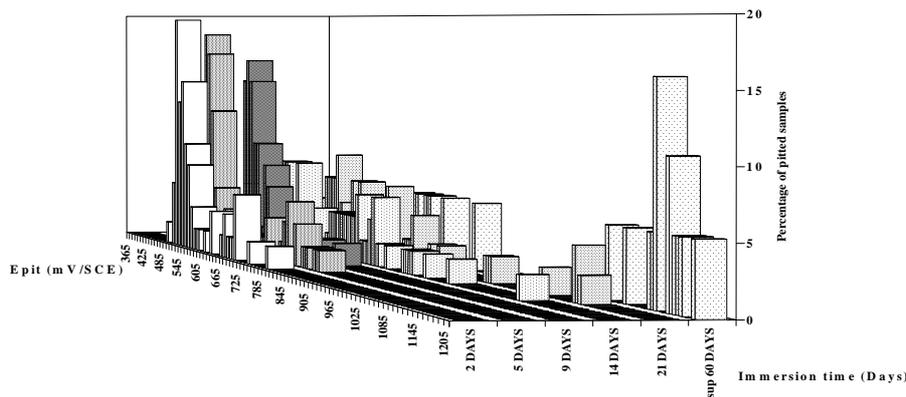


Figure 6: Influence of the immersion time on the distribution of pitted samples over the pitting potential ranges.

Crevice Corrosion

As a part of the MAST project⁶², the relative corrosion resistance of several high alloy stainless steels under crevice in different European coastal waters (Mediterranean Sea (Genova), English Channel (Cherbourg), Atlantic Ocean (Brest), North Sea (Kristineberg), Baltic Sea (Trondheim)) was followed as a function of seasons. The aim of this study was to determine the effects of the hydrological and climatic conditions on the crevice corrosion of industrial stainless steels and to try to rank these alloys regarding their crevice corrosion resistance. The experimental conditions are defined in Ref. 62 and 63. The free corrosion potential was followed on ten different materials, fully austenitic gamma including UNS 31254,

32654, 08028, 08926 and 08932 and duplex austenitic-ferritic grades including UNS 31803, 32520 and 32750 and 316L grade as reference. Two series of tests were performed in all marine stations, the first one during winter and the second one during summer, for 3000 immersion hours each. During the winter test, at IFREMER, the corrosion potential evolution is the same for all coupons with an increase after 70 hours to maximum values around 440 mV/SCE. The incubation time prior to the potential raise is shorter during winter than for the summer exposure. This is due to the lower seawater temperature at the beginning of the summer test (11°C) than at the beginning of the winter test (14°C). For the same reason, the increasing rate is slightly more rapid in winter test than in summer test (3 mV/h in winter, 1.6 mV/h in summer). The free corrosion potential evolution was similar to that observed in absence of artificial crevice former. High performance stainless steels appeared to be resistant to crevice corrosion in all stations after at least 6000 hours of immersion. A slight depassivation was observed under the crevice former on a lot of coupons but without propagation.

Discrepancies appear in the 316L SS behaviour in the different stations. The Atlantic Ocean and North Sea seem to be less aggressive in comparison with the other stations. Similar results are observed in the EFC Working Party Round Robin²⁷. In fact, differences occurred in the experimental procedure of the crevice former installation, the polyoxymethylenechloride rings were tightened with a standard torque of 3 Nm except for the tests performed in the Baltic Sea (6 Nm), and the assembly was tightened immersed in the seawater in Brest and exposed to air at the others stations. This is particularly important to explain the significant variation among the 316L susceptibility to corrosion crevice in the different stations.

Feron⁶⁴ observed a strong effect of temperature on crevice corrosion results of 316L specimens; at 20 and 30°C, through wall corrosion appeared while at 40°C, only depassivation was revealed. These results were in agreement with the potential evolution; an increase was noticed at 20 and 30°C and the potential remained constant around -50 to -100 mV/SCE. Similar results were reported in literature^{35,65}.

Numerous studies⁶⁶⁻⁶⁹ indicate that marine biofilms increase the propagation rates of the crevice corrosion for alloys of poor or intermediate resistance such as S31600, S31725 or NO8904. This increase would be due to the increase in kinetics of the cathodic reaction by biofilms. The influence of biofilms on the initiation time of crevice corrosion is less clear. Zhang et al⁶⁹ affirm that biofilms statistically (large number of specimen used) decrease initiation times for both S31600 and S31725 while opposite results⁶⁶⁻⁶⁷ are related to bad precautions in experimental procedures, in particular in colonisation of control solutions. As a large dispersion of the results has been observed depending on experimental conditions, caution is advised when comparing conclusions issued from natural medium, artificial and inoculated medium.

Laboratory studies are being currently performed to develop methods which could replace long exposure in natural seawater and in order to obtain methods yielding reproducible and useful for field application results. Methods⁷⁰⁻⁷¹ using samples with crevice formers under potentiostatic or potentiodynamic control are developed for assessment of the susceptibility to crevice corrosion with or without biocide.

The most common practice in order to eliminate biofilms is the use of biocides, and particularly chlorine. In this way the biofilm effects discussed above do not occur. However, chlorine is strongly oxidising and may affect the stainless steels behaviour.

Crevice corrosion with biocide

The effects of continuous chlorinated natural and artificial seawaters at 40 °C on the susceptibility of stainless steels to crevice corrosion were followed during the MAST project⁷². The addition of chlorine, characterised by the residual chlorine content, was fixed at 0.7 ppm in order to determine the upper acceptable limit of chlorine concentration to avoid crevice corrosion attack at 40 °C.

The free corrosion potential evolution of five high alloys and 316L stainless steel plates with artificial crevices was measured for 125 days. The potential rose up to a steady state value around 600 mV/SCE after addition of 0.7 ppm residual chlorine in natural seawater and around 250-300mV/SCE in artificial seawater for all stainless steels except 316L. The maximum potential level was a function of the chlorine concentration. These potentials were higher than in unchlorinated natural seawater. The behaviour of 316L was very different due to a very rapid nucleation of corrosion induced by the chlorinated seawater and the high temperature. In this latter case, the free corrosion potentials remained from the beginning of immersion around -100 mV/SCE. For long exposure (3000 hours) in natural and artificial seawater with 0.7 ppm residual chlorine, only depassivation with changes of colour were observed for most of the stainless steels, except important crevice corrosion on all coupons of 316L and one attack of crevice corrosion for one UR B26 coupon (in artificial seawater). But generally, the exposure in artificial seawater seems to be less aggressive according to the lower potentials reached, confirmed by the results in Table 1 and the weight losses of 316L which were less severe in artificial seawater.

UNS	Trade Name	Exposure time Hours	Natural seawater + 0.7 ppm residual chlorine	Artificial seawater + 0.7 ppm residual chlorine
32654	654 SMO	830	-	
		3000	1/3 D	-
31254	254 SMO	830	1/3 D	
		3000	1/3 D	-
31603	316L	830	3/3 C	
		3000	3/3 C	3/3 C
32550	UR 52N+	830	2/3 D	
		3000	3/3 D	-
N08926	UR B26	830	-	
		3000	1/3 D	1/3 C
-	UR B66	830	-	
		3000	1/3 D	-

Table 1: Crevice corrosion results,

D: Depassivation without weight loss, C: Crevice corrosion with weight loss, -: no attack, Number of corroded coupons/Total number of coupons.

MICROBIAALLY INFLUENCED CORROSION (M.I.C.)

Numerous industrial areas using natural seawater or fresh water with or without chloride content may be concerned by the Microbially influenced corrosion, MIC, such as: oil and gas industry⁷³⁻⁷⁴, ship hulls, water treatment plants⁷⁵, paper industry⁷⁶, food industry, nuclear industry⁷⁷⁻⁷⁹, heat exchangers⁸⁰ to mention a few. A large description of corrosion cases attributed to MIC processes on different materials and especially on stainless steels are given in the literature and in well documented reviews^{1,51,81}.

Stainless steels corrode according to known electrochemical mechanisms. The most important difference in natural seawater is the presence of a biofilm at the passive film-solution interface which may lead to local corrosion effects on SS by acting indirectly. Different mechanisms^{51,81} are proposed to explain the MIC processes:

- formation of concentration cells (O₂, pH, metallic salts...)
- production of aggressive metabolites by bacteria (inorganic or organic acids, sulphide ions,...)
- kinetics modification of the cathodic reduction reactions.

Up to now, the mechanisms involved in MIC are not fully understood and caution must be paid to corrosion problems in natural seawater; the presence of bacteria does not necessarily increase and/or accelerate localised pitting of stainless steels⁸².

CONCLUSIONS

Among the consequences of biofilm settlement on stainless steels behaviour in natural seawater, a few conclusions can be drawn:

- The kinetics of the electrochemical processes are altered: a general agreement is reached on the ennoblement of the free corrosion potential and on the modification of the cathodic activity with immersion time in natural seawater. Understanding of complex mechanisms is still subject to investigations. However, classical techniques such as E_{corr} measurements are not sufficient to solve the problem. Combinations of electrochemical techniques (Rotating Disk Electrode, Rotating Ring Disk Electrode, Scanning Vibrating Electrode, Impedance Spectroscopy...), surface analytical (X-ray Photoelectron Spectroscopy, Auger Spectroscopy, Photoelectrochemistry), microbiological and microscopical techniques should permit to simultaneously follow the ageing of passive films, the biofilm settlement and its activity, the evolution of electrochemical parameters and should be more conclusive.

- Modifications in the passive film with ageing time is responsible for the E_{corr} increase in artificial seawater.

- The corrosive nature of natural seawater compared to artificial seawater has been proved. However to avoid any confusion, care must be paid on used experimental methods (in particular, the sterilisation).

- Based on the different hypothesis, it seems unlikely that a sole explanation would be sufficient to explain the high ennoblement of E_{corr} in natural seawater. A combination of different mechanisms is probably involved in the electrochemical behaviour of stainless steels.

- The elementary pitting probability per unit area, evaluated from a statistical point of view, is strongly affected by ageing time in seawater and the open-circuit potential values.

- Discrepancies appear in the crevice corrosion behaviour of 316L SS as a function of sites. However, a large dispersion of experimental conditions are observed.

- Good behaviour is noticed during crevice corrosion tests in natural seawater and chlorinated seawater for all high performance stainless steels tested, except a slight depassivation observed under the crevice former on some coupons but without propagation.

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