Corrosion fatigue of stainless steel in tropical seawater

**J. González-Sánchez**¹ and **N. Acuña**¹,²

¹Centro de Investigación en Corrosión (CICORR), Universidad Autónoma de Campeche, Av. Agustín Melgar s/n, Colonia Buenavista, San Francisco de Campeche, Cam., CP 24039, México; ²Sabbatical Position, Universidad Anáhuac-Mayab. Km. 15.5 Carr. Mérida-Progreso, Desviación a Dzibilchaltún Cordemex, Mérida, CP 73000, México

**Abstract**

The Gulf of Mexico (GOM) is a strategic, vast region that is home to numerous marine structures. Duplex and austenitic stainless steels (SS) are potential materials for critical components in offshore drilling and production platforms as well as for oil transportation. Investigations carried out at the Centro de Investigación en Corrosión (Centre for Corrosion Research) in Campeche, México, about...
the corrosion fatigue (CF) behaviour of austenitic stainless steels in the sea of the GOM are presented here.

Emphasis is made on the application of electrochemical sensitive methods to study the early stages of damage. The stress state and the stress concentration around potential crack initiation sites were of paramount importance for the studies carried out. CF tests were mainly conducted under constant amplitude cyclic loading, stress ratio R = 0 and low loading frequency in natural seawater of the GOM in the coast of Campeche which is located in the Yucatan peninsula at the southeast of Mexico. The analysis was focused on both, crack nucleation sites and short fatigue crack growth, using two high sensitive electrochemical techniques: Electrochemical Noise Analysis and Scanning Reference Electrode Technique (SRET). It is worth mentioning that it was possible to determine the moment when the transition from corrosion pit to short fatigue crack took place in terms of electrochemical activity. Measurements of EN, showed a good relationship between the potential transients and current fluctuations with the initiation and growth of inter-granular CF cracks.

The amplitude and frequency of potential transients and the intensity of current transients became more intense as the number of loading cycles increased. SRET measurements indicated that the transition from corrosion pit to short CF crack involved a decrease of localised current density emanating from the active corrosion pit. SRET gives the possibility to follow in real time the progress of localised dissolution due to the assessment of localised anodic current emanating from perfectly located sites.

Introduction

The Gulf of Mexico is a large extension of territory that embraces the Mexican estates of Tamaulipas, Veracruz, Tabasco, Campeche and Yucatán involving 5,100 km of coast. In this area and offshore, about 80% of Mexican petroleum is produced and exported. In addition there are other industries, such as seafood processing, manufacturing, chemical processing, metallurgical industries, textile, pulp and paper processing.

Stainless steels are an important group of materials for seawater applications. This kind of “more resistant material” was introduced with the aim of reducing maintenance costs involved with materials such as carbon steel having internal and external linings and coatings. However, there are several cases around the world, from the North Sea area [1], to the Gulf of Mexico [2], in which the failure frequency in seawater of stainless steel piping systems on offshore platforms is very high, resulting in unacceptable maintenance costs.
In seawater applications, the most widely used stainless steel grade, namely, 316L, suffers from localised corrosion and is frequently affected by pitting and crevice corrosion.

Even though there is a substantial amount of data published, which documents studies of localised corrosion of 316 and 316L stainless steels, the problem of structural failure in marine environments remains. Unfortunately the degradation process is more complex than just localised electrochemical reactions at the metal surface. Failures of real structures in marine environments are induced by the effect of stresses and the corrosive environment. The stresses can be mechanically applied (constant or cyclic), residual, and in some cases, thermal which depend on the operation conditions of the component or structure.

It is documented [2-4] that the corrosion of stainless steels (SS) is more severe in natural seawater than in sterile or synthetic seawater and there is agreement among researchers that the increased corrosion is due to biofilm formation. Electrochemical reactions are influenced by the chemical micro-environments generated by formation of biofilms at the metal surface as will be presented in detail later in chapter 7 [2,5].

On the other hand there is an increasing demand for an understanding of the effects of complex load history on fatigue lifetime of components subjected to variable amplitude loading. The accumulation of damage during the fatigue lifetime of a component depends not only on its load history, but also of the synergistic effects of stress and surrounding environment [6,7].

The total fatigue life of a structure or component is often evaluated in terms of two stages: crack initiation and propagation. A more detailed characterisation of fatigue life considers the process of failure as: crack nucleation, small crack growth, macro-crack growth and final failure [8].

Corrosion fatigue is defined as a synergistic effect in which corrosion and fatigue occur simultaneously. The combined effect of an aggressive environment, such as seawater, with a cyclic stress or strain is invariably more severe than the sum of the two effects of corrosion and fatigue acting separately. It has been shown that many corrosion fatigue failures of stainless steels in seawater are induced in the early stages of damage by corrosion pits [9,10].

Pitting corrosion on stainless steels is a peculiar form of localised corrosion because most of the material is in fact not corroding; i.e., it is passive and stable [11,12]. Temperature, pH, oxygen concentration and biological activity also play an important role on the pitting corrosion process and, as a consequence, in the corrosion fatigue lifetime of structures constructed using SS [2,3,5].
The localised nature of pitting corrosion and corrosion fatigue initiation make necessary the use of increasingly sensitive electrochemical techniques such as Electrochemical Noise and Electrochemical Scanning Techniques. These techniques have been applied to the study the early stages of corrosion fatigue cracking [6,10,13]. Using SRET for example, it has been possible to measure localised pitting current densities and potential profiles during pitting corrosion of 304 SS in natural seawater [14]. SRET methods provide spatially resolved measurements and therefore have the advantage of improving the quantitative characterisation and understanding of localised corrosion.

Corrosion Fatigue (CF) is a degradation process, which involves the synergistic effect of electrochemical reactions (reactions in which charge transfer takes place at the metal - electrolyte interface), and mechanical cyclic loading (fatigue).

CF is the successive stages of metal damage that evolve with accumulated cycling loading, in an aggressive environment compared to inert or benign media, and resulting from the interaction of irreversible cyclic plastic deformation with localised electrochemical dissolution. The most complicated aspect of CF is the “combined” nature of the process, as it has been shown by Gangloff [15] that neither cyclic stress in air nor environmental attack applied separately produces the same damaging results as that of the simultaneous action.

It is generally suggested that the presence of an aggressive environment enhances both crack initiation and crack growth for a number of specific metal-environment systems when subjected to cyclic loading [16].

Corrosion fatigue has been recognised since the beginning of this century as a principal mechanism for material damage during service. The emphasis of much of the earlier work was placed upon the S-N behaviour, which is dominated by the initiation phase [17].

The majority of observed fatigue failures are in fact CF failures, since only fatigue occurring in an absolute vacuum could be termed as “pure fatigue.” The study of the fatigue damage of components and structures operating in corrosive environments is imperative, as it is known that such environments reduce the fatigue strength far below the typical fatigue strength determined in air [18-20]. In some cases the environment eliminates the fatigue limit associated with air fatigue performance as represented schematically in figure 1.

The analysis of the fatigue behaviour of metals and alloys in aggressive environments is much more complicated than that of the (in-air) fatigue damage process. An interesting result obtained by Cowley et al [21], shown in figure 2, indicates that for high cyclic stresses, a solution of 10% sulphuric
acid promotes a longer fatigue life for a stainless steel at open circuit potential when compared with its fatigue life in air. When the cyclic stress was decreased they observed failure for corrosion fatigue while the fatigue test in air did not show failure after $10^8$ cycles. That behaviour can be due to retarded crack initiation as a consequence of the tip crack blunting.

In some metal-environment systems the combined effect of corrosion and cyclic loading has been shown to produce cracks from corrosion pits and pits have frequently been the source of cracks, for example on aircraft components operating in fleets. Once a pit or group of pits is formed, the rate of pit growth is dependent mainly on the material, environment, and on the type and state of stress. Therefore, to estimate the total corrosion fatigue life of a component, it is of great importance to develop realistic models which

![Figure 1](image1.png)

**Figure 1.** Schematic of a S-N curve presenting air fatigue and CF behaviour.

![Figure 2](image2.png)

**Figure 2.** Air and corrosion fatigue S-N curves for 18Cr-10Ni-Fe alloy in 10% $\text{H}_2\text{SO}_4$ under different environmental conditions [21].
take into account the early stages of damage, including corrosion dominated processes, i.e., pitting. These models can be used to formulate methods by which designers can know and assess the effect of pitting corrosion on the fatigue life of components and structures, and apply that information during the design work.

With the intention of understanding and controlling the phenomenon of CF failure, some models based on pitting corrosion fatigue (PCF) mechanisms have been proposed in the past and some others are emerging which will be presented later in this chapter.

While it has frequently been stated that any metal or alloy that presents corrosion in a particular environment will also exhibit corrosion fatigue, such behaviour although supportable, cannot be generalised. It is not possible to establish a simple correlation between the extent to which different environments provoke different amounts of corrosion upon a given material and their relative influence on the fatigue lifetime. Corrosion reactions may enhance crack growth if they produce metal dissolution at the crack tip maintaining crack sharpness or promoting the easy transport of hydrogen into the metal for those metals that are susceptible to hydrogen induced damage [22]. The aggressive environment acting simultaneously with cyclic loading promotes an increase in the density of cracks when compared to that observed in air.

CF cracking is also considered to consist of two principal stages like the process of air fatigue, namely crack initiation and crack propagation. The initiation stage, the period required for the nucleation of cracks has been estimated to be 10 per cent of the total lifetime, whereas it is around 90 per cent for the case of air fatigue [23]. The term 'initiation stage', is in some way an ambiguous concept as in fact such term refers to a period that a defect takes to attain a detectable size. The minimum detectable size, and as a consequence the duration of this period as a fraction of total life, is a function of the method used to detect the defect. The second stage, which corresponds to crack propagation, presents perturbations in the growth of short cracks due to microstructural obstacles such as grain and phase boundaries. This anomalous behaviour only continues to a certain crack length after which the crack growth rate may have a linear relationship with the crack length [6,15].

In both fracture processes, air fatigue and CF, macroscopic cracks are termed long cracks and the initiation and growth of microscopic cracks in the sub-millimetre range precedes their formation. The latter are termed short cracks and their growth can occupy the major percentage of the fatigue life.

During the CF process, the damage accumulates with increasing the number of load cycles (N) in the following stages [24]:

1. Cyclic plastic deformation,
2. Microcrack initiation,
2.1 Corrosion fatigue crack initiation can be the result of pitting,
3. Short crack growth up to coalescence,
4. Macrorack propagation and
5. Failure of the component.

The mechanisms for CF may involve hydrogen embrittlement; film rupture, dissolution and repassivation; enhanced localised plasticity; interactions of dislocations with surface dissolution, films or adsorbed atoms; and complex combinations of these processes [24,25]. The contribution of each mechanism is controversial and depends on metallurgical, environmental and chemical conditions.

Theories of corrosion fatigue have generally relied on one or more of the following mechanisms [25-30]:
1. Stress concentration at the base of hemispherical corrosion pits created by the interaction with the aggressive environment.
2. Electrochemical attack of plastically deformed areas of metal with non-deformed areas acting as cathode.
3. Dissolution of the metal due to the rupture of the protective surface film.
4. Surface energy reduction of the metal produced by adsorption of species (principally atomic hydrogen).

Considering that CF crack initiation of components in an aggressive environment can take place by pitting corrosion, next we present in some detail the PCF mechanism.

Pitting is considered as a major mechanism for CF crack initiation in stainless steels in contact with chloride containing electrolytes. It has been proposed that for damage at smooth surfaces the process can involve the generation and growth of corrosion pits, the wedge action of corrosion products, dissolution and passivation of crack surfaces, as well as the interaction and coalescence of multiple cracks [7,9,16-20,24-27,31]. Congleton et al [22] provided evidence of crack initiation associated with the pitting corrosion process where corrosion pits were seen very easily on the surface of the metal when this was subjected to CF conditions.

Pitting corrosion in metals and alloys in aggressive environments undoubtedly does lead to a reduction in fatigue life. However, it is important to note that the corrosion fatigue phenomenon also occurs in environments where pitting corrosion does not occur. For examples, fatigue tests carried out in 3% NaCl solution adjusted to pH 12 with NaOH, where only a few randomly distributed pits were found, showed fatigue limits very similar with those observed in air [29]. This behaviour is perhaps expected since corrosion pits formed in carbon steel in these conditions tend to have a hemispherical geometry and the stress concentration they induce is not very high.
In many materials including stainless steels, corrosion fatigue crack initiation is promoted by any surface defect that has the characteristics of a real stress concentrator. Mechanical notches are more dangerous in corrosive environments than in air fatigue, and the development of corrosion pits is particularly deleterious.

Quian and Cahoon [32] demonstrated that cyclic plastic deformation accelerates both the dissolution of slip steps and the pit initiation in 316L SS in chloride containing solution. The same authors suggested the mechanism of pitting corrosion and preferential dissolution of slip steps, in which groups of small crystallographic pits form and coalesce resulting in the creation of small cracks. However, it is clear today that the presence of surface defects or pits is not necessary, as indicated by Magnin [33] who showed how the environment promotes CF crack initiation by enhancing the localisation of plastic strain.

A very important aspect of the corrosion fatigue damage process for ‘defect’ free surfaces of metals susceptible to pitting corrosion subjected to CF conditions is the transition from corrosion pit to short crack. This transition step, which can be considered as the moment at which a crack is completely established at a pit site, is believed to have a noticeable effect on the resulting fatigue lifetime. The transition point depends on the applied stress level, the nature of the environment, the pit depth and on the loading frequency as demonstrated by Akid [34]. This author suggested that a model to determine the time for a pit to develop into a crack must incorporate both frequency and stress terms.

For a given metal-electrolyte system that develops corrosion fatigue cracks from pits, the stress-assisted dissolution enhances the crack development and reduces the influence of the microstructure on crack growth. Much of the investigations carried out on fatigue and CF have focused on the behaviour of long cracks, though it is now well known that under specific circumstances fatigue lifetime is controlled by the nucleation and growth of microscopic defects [15,35].

More recent investigations [9,36] have shown that non-metallic inclusions play a very important role in the corrosion fatigue process during the initiation stage of cracks. Pits develop from electrochemical-active sulphide containing inclusions in the metal, whereas during the growth stage, corrosion tends to overcome the inherent resistance of the microstructural barriers, which in the absence of corrosion retard crack growth.

The characteristics of tropical-humid climates induce a more aggressive condition for the fatigue and CF life of engineering materials. Higher average temperature and salinity along with intense marine micro and macro-biologic activity have remarkable effect on the CF of many engineering materials. Of paramount importance is the performance and safety of engineering alloys
used to manufacture structures and components in marine applications such as offshore platforms, on shore industry, communications and electricity distribution systems.

In the tropical seawater of the Gulf of Mexico, samples of steel UNS S31603 were susceptible to localized attack generating pitting corrosion after just two days of immersion [37].

Table I shows the physicochemical properties of natural seawater at Puerto Progreso located at the northwest of the Yucatán Peninsula in the Gulf of Mexico and those reported for the North sea in Trondheim, Norway [37,38].

As can be observed, the salinity, conductivity and temperature of seawater are higher at tropical-humid climates than at North Sea whereas the pH and dissolved oxygen concentration are lower in the Gulf of Mexico.

Along with the UNS S31603, corrosion resistant alloys, UNS S31803 and N08367 were tested in natural seawater of the Gulf of Mexico (GOM) and the most active open circuit potential (OCP) values were for the steel S31603 as shown in figure 3.

Table I. Physicochemical parameters of natural seawater in the Gulf of Mexico and North sea [37,38].

<table>
<thead>
<tr>
<th></th>
<th>Gulf of Mexico</th>
<th>North sea</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salinity (ppt)</td>
<td>36 – 41</td>
<td>34 - 35</td>
</tr>
<tr>
<td>Conductivity (S cm⁻¹)</td>
<td>0.059 - 0.062</td>
<td>0.044 – 0.051</td>
</tr>
<tr>
<td>Dissolved oxygen (mg l⁻¹)</td>
<td>4.32 - 6.34</td>
<td>6.5 – 8.5</td>
</tr>
<tr>
<td>PH</td>
<td>7.2 - 8.3</td>
<td>8.15 – 8.3</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>20 – 32</td>
<td>11 - 16</td>
</tr>
</tbody>
</table>

![Figure 3](image-url). Open circuit potential vs time for N08367, S31803 and S31603 steels exposed to GOM natural seawater [37].
The results presented in figure 3 clearly demonstrate that the S31603 stainless steel had a more active OCP than S31803 (Duplex) and N08367 steels. After 15 days of exposure this steel reached an OCP around -20 mV vs SCE even several corrosion pits were observed on its surface.

When these steels were subjected to CF conditions in the same electrolyte, the OCP for the S31603 steel was also the most active as presented in figure 4. Cyclic loading induced more active potential values when compared to those for samples at unstressed condition.

The three steels immersed in natural seawater of the GOM showed that the initial stages of damage are influenced by microbial activity which induces pitting corrosion. Microorganisms are able to modify the corrosion potential of SS immersed in natural seawater and also to accelerate the breakdown of the passive layer and the formation of pits.

Such effect was observed through the lower pitting potential (E\text{pit}) values when compared with those reported in artificial seawater [39,40]. This aspect of corrosion damage in marine conditions will be presented in detail in chapter 7.

Potentiodynamic polarisation conducted on samples of S31603 steel under CF conditions and free from stress showed the effect of cyclic loading on the electrochemical behaviour of the steel as shown in figure 5 [40,41].

This figure shows that the pseudo-passive current of the steel increased four orders of magnitude when the samples are subjected to cyclic loading.

The stress amplitude seems to have an effect on the anodic behaviour of the steel as the samples under fatigue conditions with stress amplitude $\sigma_{\text{MAX}} = 140$ MPa, suffered more damage that the one under CF at stress amplitude $\sigma_{\text{MAX}} = 180$ MPa.

![Figure 4](image.png)

**Figure 4.** Open circuit potential vs time for samples under CF conditions in GOM natural seawater.
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Figure 5. Potentiodynamic curves of S31603 steel samples after $2.16 \times 10^5$ CF cycles in natural seawater under two different stress ranges [41].

Figure 6. SEM images of the CF damage on S31603 steel samples after in seawater after different number of loading cycles [41].

Figure 6 shows a sequence of CF damage on S31603 steel samples under stress amplitude $\sigma_{\text{MAX}} = 140$ MPa after A) 28800, B) 100800, C) 158400 and D) 216000 cycles.

In natural seawater, microorganisms normally colonise surfaces immersed in this media independently of the surface roughness. Microscopic
analysis of stress free S31603 steel samples immersed in natural seawater showed the presence of microorganisms adhered to the surface in an irregular distribution forming micro-colonies with a density of approximately 45000 cells/mm² after 15 days of exposure [41].

Samples under static stress (\(\sigma_{\text{Appl}} = 180\) MPa) immersed in natural seawater presented a biomass density very similar to that for samples free from stress. Cyclic stress promoted the instability of the bio film attached to the surface. The cyclic bending induced local tension and shear stresses superior than the adhesion resistance of the extracellular polymers products, promoting their detachment and consequently the colonies are ruptured and removed from the surface.

The principal effect of the microbiological activity is to reduce the pitting corrosion resistance of the stainless steels, as demonstrated by studies of the behaviour of UNS S31603 steel immersed in natural and sterilised seawater. The open circuit potential (OCP) for this steel as a function of time showed to be more active for tests using sterilised seawater reaching values of -150 mV vs saturated calomel electrode (SCE).

The tendency to more positive values for the OCP is related to the microorganisms colonisation on the metallic surface. The pitting potential of stainless steels is also affected by the presence of microbial activity on their surface reaching values from +100 to +300 mV vs SCE. The susceptibility of stainless steels to suffer pitting corrosion increases if the corrosion potential is very near to the pitting potential [37].

Pitting corrosion enhanced by biological activity on the surface of the S31603 steel has great influence on the mechanical behaviour of this metal when subjected to CF conditions. CF studies carried out at the GOM in Yucatán and in Campeche showed that initially hemispheric pits transform to a hemi elliptical shape as consequence of the applied stress. These corrosion pits eventually transformed to CF cracks.

Studies carried out on samples of S31603 SS subjected to CF conditions in artificial seawater showed that corrosion pits after nucleation took a shape and growth direction related to the direction of the maximum applied stress and acted as real stress concentrators [42]. Figure 7 shows the micrograph of the surface of a sample of S31603 stainless steel subjected to CF at \(R = 0.0\), \(f = 0.17\) Hz, \(\sigma = 190\) MPa.

In this case cylindrical tubular samples were subjected to cyclic internal pressure which induced circumferential and longitudinal strains in the sample. Such a configuration promoted pit growth and coalescence forming like-crack defects of about 20 to 30 µm long orthogonal to the direction of the circumferential induced stress.
As indicated by Qian et al. [32], small groups of crystallographic pits formed and coalesced creating small cracks in Austenitic SS in sodium chloride solution at open circuit potential.

The same author stated that plastic deformation apparently accelerated pit initiation within the slip bands at stress levels higher than the yield stress but no information was given about the electrochemical activity of the corrosion pits involved.

The authors of this chapter have used sensitive electrochemical techniques to study the early stages of CF cracking. Electrochemical noise and scanning reference electrode technique measurements have been applied on samples of S31603 SS subjected to CF conditions in natural and synthetic seawater [41,42]. Measurements of potential and current noise were conducted using a WE1-WE2-RE arrangement with two nominally identical S31603 steel working electrodes (WE1 and WE2) in natural flowing seawater and a saturated calomel reference electrode (RE).
Two cases of study were considered as follows: a) two stress free identical working electrodes; and b) one working electrode under cyclic stress and the other one free of stress. The WE1 and WE2 specimens were coupled in a freely corroding system using the conventional ZRA mode for current and noise measurements.

The saturated calomel electrode (SCE) was positioned very close to the exposed specimens by using a luggin capillary, in order to measure the $E_{corr}$ and its fluctuations.

The potential and current fluctuations as a function of time were recorded at intervals $\Delta t = 0.5$ s. Fatigue tests were conducted by applying cyclic bending with a triangle waveform at constant stress amplitude in a homemade device. The loading frequency was of 0.17 Hz, the stress ratio $R = 0$, and the maximum stress $\sigma_{MAX} = 140$MPa (60 % $\sigma_{ys}$).

The potential and current time series resulted from free stress samples at open circuit potential after three, six and ten days of exposure in flowing natural seawater are shown in Figures 8-10, which show the correlation between the potential and current transients. After three days of exposure, potential transients were observed, with a pattern of quick drop and slow recovery. The amplitude of the fluctuations of potential and current density varied from 4 to 20 mV with associated current density from 0.05 to 0.20 mA cm$^{-2}$ for three days of exposure; 10 to 40 mV with associated current density from 0.05 to 0.25 mA cm$^{-2}$ for six days; and finally from 10 to 60 mV with associated current density from 0.05 to 0.30 mA cm$^{-2}$ after ten days of exposure.

A common characteristic pattern of quick drop and slow recovery was observed from measurements carried out after three, six and ten days of exposure under unstressed condition.

**Figure 8.** Potential and current time series for S31603 SS exposed to natural seawater during three days free of stress.
Figure 9. Potential and current time series for S31603 SS after six days of exposure to natural seawater free from stress.

Figure 10. Potential and current time series for S31603 SS after ten days of exposure to natural seawater free from stress.

Common explanations for these transients have been associated with nucleation, temporary growth and repassivation of micropits [43]. No significant differences were observed in the amplitude of the fluctuations of potential and current density for the different periods of immersion in seawater; however after ten days under CF conditions the frequency of current density and potential fluctuations was much higher than those generated at the beginning of the test. We propose that this behaviour could be associated with an increment of localised attack events, such as metastable pitting corrosion, as is corroborated through SEM images.

Current density and potential fluctuation patterns of quick drop and slow recovery have been also related to anodic dissolution, passive film breakdown, crack initiation and crack growth [44].

During the CF tests conducted in natural flowing seawater, the WE1 was undergoing cyclic stress from 0 to 140 MPa, while WE2 acted as a stress free counter electrode. The potential noise had a characteristic pattern of quick drop and slow recovery. For the CF conditions, corresponding potential and current time series after three, six and ten days are shown in Figures 11-13 [10].
Figure 11. Potential and current time series for S31603 SS after three days of exposure to natural seawater under CF conditions [10].

Figure 12. Potential and current time series for S31603 SS after six days of exposure to natural seawater under CF conditions [10].

Figure 13. Potential and current time series for S31603 SS after ten days of exposure to natural seawater under CF conditions [10].

The electrochemical noise patterns from samples under CF conditions for cyclic stress from 0 to 140 MPa could be related to the development of intergranular small fatigue cracks as observed in the SEM images of figure 6. After 10 days under CF conditions large intergranular cracks were observed 6D.
In the above mentioned work, the crack growth rate was not measured, however, after six days of exposure; small cracks around 400 µm long had grown from nucleation sites. The accumulated plastic deformation due to cyclic loading induced from since the beginning of the tests, the growth of cracks by interconnection of several small cracks following the grain boundary pattern as shown by figures 6B, 6C and 6D.

Crack nucleation and the early stages of crack growth could be associated to patterns of quick drop and slow recovery in the current density time series with current density fluctuations from 0.10 to 0.60 mA cm\(^{-2}\). The Faradaic contribution of long intergranular CF crack growth can be associated with potential and current density fluctuations of about 200 mV and 8.0 mA cm\(^{-2}\) respectively.

The microstructural condition of the stainless steel S31603 definitely promoted the preferential crack growth along the grain boundaries and also intergranular corrosion in natural seawater when subjected to CF conditions. Simple analysis of electrochemical noise results in this stage was not enough to propose a base mechanism for the CF cracking under the experimental conditions used.

The methodologies used up till now to study the initial stages of CF damage through EN measurements have been unable to separate the contribution due to localised corrosion from that due to crack nucleation and growth. Crack nucleation and growth involve generation of fresh active metal surfaces which interact with the electrolyte and induce changes in the amplitude of the anodic current noise signals. This contribution to the noise signal must be different from that associated to the localised corrosion process which in principle should have dissimilar nature. Pitting corrosion studies conducted in the past using the electrochemical noise technique considered that the observed high amplitude oscillations associated to the breakdown and recovery of passive layers had a totally stochastic nature. Succeeding studies demonstrated that such approach was not correct and that the fluctuations observed during the pitting corrosion of iron have a non-linear chaotic nature, this means processes of complex dynamics that are very sensitive to initial conditions [45,46]. In a relevant work, Zhai et al., demonstrated the synchronisation of active sites which generated chaotic electrochemical fluctuations similar to those observed during pitting corrosion [47]. While this characteristic is now well established for localised attack no similar behaviour has been observed during environmental induced cracking like stress corrosion cracking and CF.

Research work carried out at the Centre for Corrosion Research (Universidad Autónoma de Campeche, México) by the authors has been devoted to elucidate the electrochemical and mechanical conditions for the
transition from corrosion pit to short CF crack and during the early stages of crack. Using recurrence plots to analyse electrochemical current noise signals we were able to distinguish changes in the dynamics of the CF process due to short CF crack growth and also due to pitting corrosion [13].

Recurrence plots (RPs) is a novel and powerful methodology for assessing the geometry of the dynamics exploiting non-linear dependencies even in non-stationary time-series. These plots disclose distance relationships between points on a dynamical system providing a faithful representation of the time dependencies (correlations) contained in the data [13,48]. This is a graphical tool for the diagnosis of drift and hidden periodicities in the time evolution of dynamical systems, which are unnoticeable otherwise.

An important and simple aspect that must be considered when using and studying recurrence plots (RP’s) is: If the signal under analysis is truly random and has no structure, the distribution of colors over the RP will be uniform, and so there will not be any identifiable patterns. On the other hand, if there is some determinism in the signal generator, it can be detected by a characteristic distinct distribution of colors. For example, the RP obtained from a sinusoidal time series is as shown in figure 14.

Considering this, the length of diagonal line segments of the same color on the RP can give an idea about the signal predictability [50-52]. To quantify complex structures that occur in RPs, Webber proposed several options in a seminal paper [52] that constitutes the recurrence quantification analysis (RQA). For the present work the parameter of RQA considered was the Percent of Determinism (%D) which is the calculated as follows:

\[
\%D = \frac{D_{\text{Recurrence}}}{N_{\text{Recurrence}}} \tag{1}
\]

![Unthresholded Recurrence Plot of a Sinusoidal time series](image)

**Figure 14.** Unthresholded Recurrence Plot of a Sinusoidal time series [49].
DRecurrence is the number of points that constitute line segments parallel to the square bisector of the recurrence plot. A line segment is defined as two or more adjacent points. NRecurrence is the total number of recurrence points in the superior triangle of the recurrence plot without counting the number of points on the bisector [50,51].

When we applied this methodology to analyse current time series from electrochemical noise measurement during CF test of S31603 stainless steel in natural seawater of the Gulf of Mexico it was possible to separate the contribution of pitting corrosion which electrochemical oscillations presented a %D higher than 80%, from the CF crack initiation to which we associated a stochastic behaviour due to low %D of about 5%. This separation was possible by the use of the recurrence quantitative analysis parameter (RQA) selected: the percentage of determinism %D as shown in figure 15 [13].

![Figure 15. Percentage of determinism (% D) as a function of the Number of cycles (N) for samples under CF conditions (■) and samples without cyclic stress (□) [13].](image)

Considering the results obtained from CF tests it could be suggested that the moment for the CF crack initiation and growth involved a totally stochastic distribution which induced the sudden and remarkably decrease of %D. Low values of %D characterise stochastic processes that in the present case can be related to the Faradaic contribution of the CF crack initiation. CF cracks involve the creation of new active metallic surfaces which can grow to stochastic rates and directions.

Recursive Plots RPs applied to the analysis of electrochemical current noise measured during CF tests and their assessment by (RQA) represents a powerful non-linear analysis tool as it allowed us to establish clearly the dynamics of the early stages of CF cracking.
Considering that electrochemical dissolution of metals during localised corrosion takes place at permanently separated sites from the cathodic areas, this gives the possibility of direct measurements of the cathodic and anodic reactions through \textit{in situ} non-intrusive studies. Measurements of the physical separation of anodic and cathodic areas, the currents flowing between them as well as the mapping of potentials in electrolytic solutions have been successfully used for the study of the processes of localised corrosion of different systems [14,53-55].

In 1966, with the aim of determining the velocity of metal dissolution directly in the operating pits during pitting corrosion, Rosenfeld and Danilov [54] designed an apparatus to measure the field strength in the electrolyte directly above an active pit. They employed a twin probe method by using two reference electrodes, which makes it possible to measure the potential difference $\Delta E$ in any direction between two points in the electrolyte with the aid of two non-polarisable electrodes, for example calomel electrodes. With the measurement of the electric field strength in the electrolyte over the pits it was possible to determine the current flowing from the anode points, based on a well-known fact. This fact establishes that, the vector of the normal component of the current density at a pre-determined point ($i$) in a uniform field is equal to the product of the electric field strength $E$ and the specific conductivity of the medium $\kappa$.

The method used by these workers was a scanning reference electrode technique (SRET), but at that stage of development the method had some limitations. Nowadays SRET is a non intrusive electrochemical technique capable to assess in real time changes in localised electrochemical activity although its sensitivity is limited.

Measurements conducted using the SRET during CF tests of UNS S31603 stainless steel in FeCl$_3$ solution showed a decrease in the localised electrochemical activity which was related to the transition from pit to CF short crack as shown in figure 16. The localised current density plotted as a function of the number of cycles was determined from area map scans recorded continuously during the cyclic loading [6,42].

CF tests were conducted on a specimen of steel S31603 in artificial seawater at free corrosion potential with a circumferential stress of 260 MPa ($\sigma_{\text{MAX}} = 1.1\sigma_{\text{ys}}$), a crack developed and produced failure after just 48000 cycles. At that stress level the failure of the specimen took place after much fewer stress cycles than expected. Qian et al. [32] reported a maximum stress for failure of 316L SS in 0.5 M NaCl at $10^7$ cycles of 250 MPa. Sedriks [56] reported values of 260 MPa also for 316L SS in 3% NaCl solution.

The SEM images in figure 17 of the crack that produced the failure of the specimen of steel S31603 show that the crack grew following pits possibly originated along a non-metallic inclusion.
SRET localised current density from pit a vs number of cycles in 0.05 M FeCl₃ solution [6,42].

Figure 17. SEM images of a 316L SS specimen after failure subjected to CF in artificial seawater at free corrosion potential, applied stress: 260 MPa ($\sigma_{\text{MAX}} = 1.10\sigma_{\text{YS}}$).

SRET measurements carried out at different periods during the CF tests did not detect localised activity that could be associated with the nucleation or propagation of the crack. From the results of the present study it is suggested that the localised events taking part in the nucleation of corrosion
fatigue cracks involve very low current densities; at least too low to be detected by the SRET instrument used here.

Magnin et al. [167] proposed a method to detect corrosion fatigue crack initiation from measurements of current density as a function of cyclic plastic strain of specimens under potentiostatic control. These authors did not consider the effect of corrosion pits as they measured the global current emanating from a large area (1.5 cm²) but the local dissolution of microcracks which, favours grain boundary crossing and the micro-coalescence of the cracks.

As mentioned previously, even though the size of the local anodes cannot be determined directly from SRET measurements, the change in electrochemical activity of pits, as a function of number of cycles may be used to define the pit-to-crack transition.

A reduction in current was observed when a crack initiated from a pit. This observation was made for cracks initiating from pits having different electrochemical activity i.e., current density. The data of SRET for the current density of the active pits can be used to calculate the pit depth at the transition to a fatigue crack.

The pit depth $P_d$, at which the pit-to-crack transition occurs, can be obtained by equation (2) proposed in the literature [41,57,58].

$$
a = \left[\left(\frac{3MI_{PO}}{2\pi nF\rho}\right) \exp\left(-\frac{\Delta H}{RT}\right) t + a_0^3\right]^{\frac{1}{3}} ; \ a \leq a_r
$$

in which:

- $a = P_d$, pit depth at pit-to-crack transition (cm)
- $M$ = atomic weight (55.845 g/mol, for Fe)
- $n$ = number of transferred electrons (2 formation of Fe$^{2+}$)
- $\rho$ = density (8 g/cm³ for SS)
- $\Delta H$ = activation enthalpy (-342 J/mol)
- $F$ = Faraday's constant (96500 C/mol)
- $T$ = absolute temperature (299 K)
- $R$ = the universal gas constant (8.3143 J/mol-K)
- $I_{OP}$ = pit current (A)
- $t$ = time for a pit to reach the size (sec)
- $a_0$ = initial pit depth (0.0001 cm)

If the value of the pit current obtained from the SRET measurement associated with the pit-to-crack transition (figure 16) for 316L SS is used in the above equation, the pit depth ($P_d$) at the moment of transition is found to be 200 µm.
The stress intensity factor range \( \Delta K_1 \) has been used \([17,59]\), to account for the role of pitting in defining threshold conditions for cracking using LEFM in the context of fatigue-limit based propagation, using equation (3).

\[
\Delta K_{th} = \alpha \Delta \sigma_{th} \sqrt{\pi a}
\]  

(3)

where \( a \) is the pit depth (\( P_d \)), \( \Delta \sigma_{th} \) is the threshold fatigue strength, \( \alpha \) is a geometric factor and \( a \) is the pit depth. For semi-circular surface cracks, \( \alpha \) is approximated by 0.67 \([17,59]\) and \( \Delta \sigma_{th} = 220 \) MPa for 316L SS in Cl\(^-\) containing solution, pH 3 \([56]\).

Using equation 3 and the pit depth (\( P_d \) at transition) obtained from equation 2, the threshold stress intensity factor range was found to be: \( \Delta K_{th} = 3.69 \) MPa\( \sqrt{m} \). The range of localised current density (at the pit-to-crack transition) for 316L SS specimens was from 200 to 350 mA/cm\(^2\). From these values of localised current and using equation 5.1 it is possible to establish a range of pit depths at which the pit-to-crack transition occurs during CF tests of 316L SS in 0.05 M FeCl\(_3\) at a \( \sigma_{MAX} = 0.77 \sigma_{ys} \).

\( P_{d,316L} \) at transition = 175 to 210 \( \mu\)m.

The values of threshold stress intensity factor range vary according to these pit depths for the pit-to-crack transition and were found to be: \( \Delta K_{th} = 3.45 \) to 3.78 MPa\( \sqrt{m} \).

The results from SRET measurements on 304 SS specimens under CF conditions in 0.05 M FeCl\(_3\) at a stress range of 200 MPa (\( \sigma_{MAX} = 0.81 \sigma_{ys} \)), indicated that the values of pit current density at the pit-to-crack transition were in the range of 180 to 250 mA/cm\(^2\). The application of equation 5.1 to the values of current density stated above gave the following range of pit depths at the transition: \( P_{d,304} \) at transition = 130 to 175 \( \mu\)m.

These pit depth values for the pit-to-crack transition are used in equation 5.2 to determine the threshold stress intensity factor range for the 304 SS.

The value of the \( \Delta \sigma_{th} \) for 304 SS in Cl\(^-\) containing solution, pH 3 used for this calculation was 200 MPa, \([15]\). The results showed that the threshold stress intensity factor was: \( \Delta K_{th} = 2.7 \) to 3.14 MPa\( \sqrt{m} \).

From studies of the effect of pitting on the CF crack nucleation, Zhou et al. \([59]\) reported values of 5.06 to 6.16 MPa\( \sqrt{m} \) for the threshold stress intensity factor range for cracks nucleated from pits of 110 \( \mu\)m depth in 12 Cr martensitic steel in 0.1 M NaCl solution. Acuña \([41]\), reported a \( \Delta K_{th} = 2.5 \) MPa\( \sqrt{m} \) for cracks nucleating at pits of 120 \( \mu\)m depth in 316L SS flat specimens subjected to bending CF conditions in natural seawater at free corrosion potential. Result from CF tests on open-hole specimens of 2024 T3
(bare) alloy in 0.5 M NaCl solution conducted by Chen et al. [60] showed that the $\Delta K_{th}$ was of the order of 2.23 to 3.63 MPa$\sqrt{m}$ for pits with aspect ratio ($c/a$) of 0.12 and 0.33 respectively.

Calculation of pit growth has been conducted in the past by using indirect methods or probabilistic models, [58]. SRET measurements on the other hand can provide direct assessment of localised current densities emanating from pits.

This technique used during the early stages of damage by CF can also overcome the uncertainty of intrusive methods for assessing the pit-to-crack transition.

**Conclusions**

In the GOM operate offshore and onshore metallic structures and components of infrastructure including refineries, petrochemical complexes, oil and gas platforms and submarine pipelines. The diverse installations and equipment require corrosion resistant alloys for critical service conditions (humid, warm, salt-laden tropical environment). Austenitic SS are prone to undergo localized corrosion and CF cracking, its magnitude and nature depending on the equipment operating conditions. Results obtained from research work carried out on corrosion fatigue of stainless steels in natural seawater in the Gulf of Mexico over the last 10 years at the Centre for Corrosion Research (Universidad Autónoma de Campeche) summarise several approaches to study the mechanism of the early stages of CF cracking.

- Austenitic SS UNS S31603 was susceptible to intergranular cracking under cyclic loading conditions with a stress ratio $R=0$ and a loading frequency of 0.17 Hz. The tests carried out under cyclic stress amplitude of 140 MPa in natural seawater indicated a reduction in the yield strength when compared with the tests under cyclic stress of 0 to 180 MPa, due to the development of surface intergranular cracks.

- Visual recurrence analysis applied to the electrochemical current oscillations registered during corrosion fatigue tests allowed us to characterise the electrochemical dynamics on stainless steel samples surface showing clearly the dynamics of localised corrosion, as well as the formation and initial growth of short CF cracks.

- It was possible to separate the contribution of pitting corrosion which electrochemical oscillations presented a %D higher than 80%, from the CF crack initiation to which we associated a stochastic behaviour due to low %D of about 5%. This separation was possible by the use of the recurrence quantitative analysis parameter (RQA) selected: the percentage of determinism %D.
• Recursive Plots RPs applied to the analysis of electrochemical current noise measured during CF tests and their assessment by (RQA) represents a powerful non-linear analysis tool as it allowed us to establish clearly the dynamics of the early stages of CF cracking.

• Despite the inability to spatially resolve either the pit or crack size from SRET measurements in FeCl₃, the change detected in electrochemical activity can be related to the transition from localised metal dissolution to crack nucleation; which may involve a redistribution of current over the new crack surfaces. The semi-quantitative assessment of pit-to-crack transition in terms of localised current density proposed in this study may be conservative, as the SRET method presents limitations. However, the use of more stable scanning electrodes, SRET calibration factors together with the measurement of pit depth in a set of parallel tests can give a more reliable assessment of the pit-to-crack transition in a semi-quantitative and non-intrusive basis.

• By using the values of pit current density obtained from SRET measurements, a critical pit depth for the pit-to-crack transition was determined from which, the threshold stress intensity factor range was calculated for the 304 and 316L SS's subjected to CF conditions in 0.05 M FeCl₃ solution. The values were, for 316L SS: \( \Delta K_{th} = 3.45 \) to 3.78 MPa√m, and for 304 SS \( \Delta K_{th} = 2.7 \) to 3.14 MPa√m.

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