CORROSION-FATIGUE PROCESS: LAB TESTS AND MATERIAL SELECTION

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ABSTRACT

Corrosion is a major issue in our industry and it is hard to predict its behavior. It depends on many factors, among which the most relevant are pressure, temperature, concentration, water, PH, chlorines and flow conditions. From the materials point of view, the most relevant parameters are the alloys (such as Ni, Cr, Nb, Mo, C), structure, YS/UTS, electronegativity, hardness and toughness. Some alloys give the steel structure certain properties, which are not only related to its mechanical properties but also to grain size, arrangements and molecular interspaces. Increased volumes of injection water/gas for mature fields and shale operations increases also the risk of failures related to corrosion processes. Tenaris makes an effort to evaluate the behavior of standard materials in aggressive environments looking for stronger steels and connections.

This paper aims to discuss the behavior of different Sucker Rods steels in corrosion and the influence of manufacturing techniques.

INTRODUCTION

Corrosion is the deterioration of a material due to the interaction with its environment. Corrosion can lead to many different consequences on the operation of equipment for the oil and gas industry and the effects are often more serious than the simple loss of a mass of metal. Failures of various kinds and the need for expensive replacements may occur even though the amount of metal destroyed is quite small.

The total annual cost of corrosion in the oil and gas production industry is estimated to be $1.372 billion, broken down into $589 million in surface pipeline and facility costs, $463 million annually in down hole tubing expenses, and another $320 million in capital expenditures related to corrosion.[1] The increasing demands in the oil and gas industry, with more difficult conditions due to several factors, such as increasing well depths, high temperature, high pressure, new techniques for recoveries, and the exploration and production of non-conventional areas, push the limits of steel products. The challenges for steel manufacturers are to develop steel products more suitable for these stringent conditions, improving the performance of the material while keeping reasonable costs and saving energy.

Tenaris is currently studying the performance of several materials under extreme conditions, in order to better understand the relationship between environmental variables and steel properties, especially for Sucker Rods. Results of this research led to the development of new steel composition and processing routes, both for sucker rods and couplings, that notably increase the performance under corrosive environments.

Corrosion can be viewed as the spontaneous return of metals to their ores. The huge amount of energy consumed in manufacturing metals into final products is the driving force for the corrosion process to occur. Corrosion of steels in oil and gas production and transportation is almost always electrochemical in nature, due to the aqueous phase normally present.

Corrosion depends on many factors, among which the most relevant from the environmental side are pH, pressure, potential, temperature, fluid flow, concentration (solution constituents) and water cut. From the point of view of the materials, the most relevant parameters are the steel chemistry, including alloy additions (Cr, Ni, Mo, Nb, V) and steel cleanliness, microstructure, mechanical properties and toughness. Design factors considering all the parameters can improve the performance. Proper steel alloying and process control are key points to achieve these goals.

AQUEOUS CORROSION

Aqueous solutions are the environments most frequently related to corrosion problems. Corrosion of steel in aqueous solution is almost always electrochemical in nature. The surface of the steel acts as an electrode, and the conducting liquid is called the electrolyte. Corrosion can be localized, e.g. forming pits, or generalized covering an extended area. For steel corrosion to occur, two reactions must concur: an oxidation reaction and a cathodic reduction. For example, the corrosion of iron in acid solution is expressed as follows:

Anodic reaction (oxidation): $Fe \Rightarrow Fe^{2+} + 2e^-$

Cathodic reaction (reduction): $2H^+ + 2e^- \Rightarrow H_2$

Overall reaction: $Fe + 2H^+ \Rightarrow Fe^{2+} + H_2$

Since electrons are liberated by the anodic reaction and consumed by the cathodic reaction, an electrochemical current is generated during the corrosion process. This current is a measure of the corrosion rate. This current will continue meanwhile the electrons released during the oxidation can pass to the metal to complete the cathodic reaction. Since the corrosion current must flow through the liquid by ionic conduction the conductivity of the liquid will also influence the corrosion process. Therefore, the interface between metal and liquid is a complete electrochemical cell.

Some factors can accelerate the corrosion rate. These include:
(a) Localized corrosion areas, where the conditions for corrosion to proceed are favored. One example is the called galvanic effect, that occurs when two metals of differing electrochemical potential are placed in electrical contact, forming a galvanic couple. Localized corrosion can also appear due to fluid turbulences, temperature variations, surface discontinuities, etc.

(b) Enhance of the anodic or cathodic reaction due to, for example, the presence of some aggressive ions. Chloride ions tend to increase corrosion rate by avoiding the formation of protective oxide layers on the metal surface.

The interaction between the steel and the environment is a complex issue dominated by a huge number of variables. The combined action of pH, temperature, oxidation power, pressure and concentration, determine the corrosion aggressiveness not only due to the effect of each variable but also for the interdependence between them. To further complicate the problem, corrosion will also depend on the steel (or other metal involved) chemistry, microstructure and properties, surface condition and also the stress field applied on the component.

CO_2 corrosion (sweet corrosion)

Extensive research[2-10] has been performed about the mechanisms of CO_2 corrosion and the effect of pH, pressure, temperature and water cut on steels. Furthermore, there are models proposed to predict CO_2 corrosion on steels based on empirical data. Carbon dioxide gas dissolves in water forming a weakly carbonic acid through hydration by water: $CO_2+H_2O \Leftrightarrow H_2CO_3$

This acid then dissociates to bicarbonate ion and further to carbonate ion:

$$H_2CO_3 \Leftrightarrow H^+ + HCO_3^-$$

$$HCO_3^- \Leftrightarrow H^+ + CO_3^{2-}$$

Since steel releases Fe^{2+} ions when corroded, at certain concentration iron carbonates will precipitate as:

$$Fe^{2+} + CO_3^{2-} \Rightarrow FeCO_3$$

The overall reaction on steel surface is:

$$Fe + CO_2 + H_2O \Rightarrow FeCO_3 + H_2$$

CO_2 corrosion is a complex phenomenon that depends on numerous variables such as pH, partial pressures, and temperature. Flow velocity and particle content is another key point to determine corrosion rate in CO_2, since erosion leads to the destruction of the protective carbonate layer. The temperature at which the rate is a maximum depends on the other variables. In some testing we have seen the maximum corrosion rate at about 60°C.

H_2S corrosion (sour corrosion) and SSC (sulfide stress cracking)

Corrosion of steels in the presence of hydrogen sulfide in aqueous solution is a major problem in the oil and gas industry. In an H_2S environment many types of iron sulfide may form such as amorphous ferrous sulfide, mackinawite, cubic ferrous sulfide, smythite, greigte, pyrrhotite, troilite and pyrite, among which mackinawite is considered to form first on steel surface by a direct surface reaction. The scale growth, one of the main factors governing the corrosion rate, is dependent on the kinetics of surface scale formation. The poorly known mechanism of H_2S corrosion makes it difficult to quantify the kinetics of iron sulfide scale formation.

Dissociation of dissolved H_2S is given by:

$$H_2S \Leftrightarrow H^+ + HS^-$$

And the dissolution of HS^- is given by:

$$HS^- \Leftrightarrow H^+ + S^{2-}$$

One of the possible resulting reactions is:

$$Fe + H_2S \Leftrightarrow FeS + H_2$$

But several other corrosion products can be formed and, under certain conditions, the H^+ ions are prevented to recombine.

In a H_2S dominated system, the direct reduction of H_2S lowers the pH of the solution as it acts as a weak acid and increase the corrosion rate by providing an extra cathodic reaction. In the absence of buffering ions, water equilibrated with 1 atm of H_2S has a pH of about 4. However, under high-pressure formation conditions, pH values as low as 3 have been calculated.

The combined effect of H_2S and CO_2 gives even more complicated mechanisms of corrosion[11,12]. When H_2S is present in low concentration in a CO_2 dominated system, the iron sulfide (FeS) film interferes with the formation of the carbonate scale ($FeCO_3$). Under turbulent conditions, removal of the protective scale will lead to an increased corrosion rate. The scale formation in the CO_2/H_2S system depends on many factors, such as H_2S and CO_2 concentrations, solution's chemistry and temperature.

Hydrogen sulfide can also play other roles in corrosion in oil and gas production. As mentioned, under certain conditions, the H^+ ions are prevented to recombine and hence do not form H2 gas. Instead, H^+ ions reduce to H atoms. Atomic hydrogen migrates through the steel microstructure to grain boundaries, inclusions and other areas of stress concentration, reducing the ductility. Under the effect of tensile stresses, from the load state or from residual stresses, sulfide stress cracking (SSC) can be promoted. The effect of sulfide stress cracking can be catastrophic, leading to a rupture with a noticeable mass loss.

Corrosion fatigue

Corrosion fatigue is the main cause of failure in Sucker Rods strings. Corrosion fatigue is the conjoint action of a cyclic stress and a corrosive environment to decrease the number of cycles to failure in comparison to the life when no corrosion is present.

The mechanism of CF may involve hydrogen embrittlement, film rupture, dissolution and repassivation, enhanced localized plasticity, interactions of dislocations with surface dissolution, films of absorbed atoms, and complex combinations of these processes. The environment may affect the probability of fatigue crack initiation, the fatigue crack growth rate, or both.

A good summary of environment effects on initiation is given by Brown[13]. In the absence of a corrosive environment the localized plastic deformation in the form of persistent slip bands (PSB's) will initiate cracks. A corrosive environment can reduce the crack initiation stage by inducing alternative initiation mechanisms. These will include:

- local galvanic activity between phases
- dissolution of metal after mechanical disruption of passive films by PSB's
- metal dissolution simply due to active sites in PSB's
- dissolution of grain boundary regions due to compositional effects, for example sensitized steels
- pitting corrosion

These all have a time component which translates into a frequency dependence in fatigue. Usually, the lower the frequency of the cyclic stressing, the more effective the corrosive environment is in decreasing the fatigue life. These mechanisms either increase the effectiveness of PSB's in initiating cracks or change the initiation mechanism completely.

In carbon steels, cracks often originate at corrosion pits, however pitting is not a prerequisite for corrosion fatigue cracking in these materials[14]. Early works, like that of Simnad and Evans[15], have mentioned this fact and also the increase of localized corrosion due to the presence of cyclic loads and local deformation[16]. Corrosion process is accelerated at freshly exposed metal surface leading to broad fissures and incipient cracks. Initiation of CF is a very complex topic, Hertzberg said "no precise definition for crack initiation has been or perhaps can be identified"[17]. Summarizing, corrosion fatigue is influenced by various mechanical, chemical and microstructural parameters that interact locally; the damage mechanisms are controversial and lifetime predictions are still empirical[18].

LABORATORY AND FIELD EXPERIENCE

Corrosion fatigue in sucker rod materials

Time-to-failure tests were used to determine the corrosion fatigue endurance limit of materials. Tests were performed in a Hastelloy autoclave that permits to reach high temperatures and pressures, in harsh environments like those encountered in oil and gas production and transportation. The machine allows to reach cycling frequencies fixing the desired combination of minimum and maximum tensile loads. Longitudinal special tensile specimens were machined from the center of the rods and grinded.

The tests were carried out in simulated production environments, at 10 bar of partial pressure of CO_2. Maximum and minimum stresses were established in order to reproduce an operation condition that caused premature field failures (less than 500,000 cycles). A simulated formation water composition used was 124g/lt NaCl and 1.315 g/lt $NaHCO_3$, with predicted pH at test conditions of 5. The solution temperature was of 60°C and the total pressure was 31 bar (reached using N2 high purity) in all tests. The maximum and minimum applied stresses were 47 Ksi and 12 Ksi respectively. The frequency of cycling was 20 cycles/min, higher than field frequency to reduce test duration but restricted taken into account that corrosion-fatigue is a time-dependant process. The time to failure (number of cycles) was determined and the failed specimens were analyzed using scanning electron microscopy.

Average results are shown in Figure 1. Since fatigue test in harsh environments is a stochastic process, a high dispersion was observed in the tests. Nevertheless, all the standard Sucker Rods grades, both D and high strength, presented a high corrosion fatigue susceptibility. Furthermore, results are in agreement with the field experience for premature failures, and the morphologies of transversal cracking were also similar to those observed in field failures (Figure 2). SEM/EDS analysis showed that in all tests corrosion products consisted mainly in iron carbonates. The type of pattern observed (transversal cracking) could be indicative of mechanic load effect on the integrity of semi-protective corrosion product films; if film is detached from the surface due to mechanical action, unprotected metal is exposed and corrosion rate increases. Analysis using SEM revealed that in some cases small cracks joined to form macro cracks. All the failures started in the surface of the specimens but since important damage was observed in initiation zone, it was not possible to determine if pitting acted as crack starter. From these results, it is evident that for corrosion fatigue to occur it is not necessary to have any discontinuity on the surface of the material.

New tests have been carried out to asses the effect of H_2S containing environments on corrosion fatigue. Furthermore, since field failures are often related to both H_2S and CO_2 bearing environments, mixed tests are being performed.

In order to compare the results with those observed in CO_2 tests, load conditions and frequency of cycling for H_2S were as described for CO_2 tests. The tests were carried out in a buffering solution (adjusted by addition of HCl or NaOH) with a pH of 4.5, at 1 bar of pressure of H_2S (1 bar of total pressure) and at room temperature. The time to failure (number of cycles) was determined and the failed specimens were analyzed using SEM. Results showed that the effect of H_2S environment is even more aggressive than CO_2. Time to failures was one order of magnitude lower than in CO_2 tests: for UHS grades, average life was in the order of 25,000 cyles, whereas for D grade, it was below 100,000 cycles.

Based on the obtained results, new steels are being designed and tested. Design factors that can be used to improve corrosion fatigue performance are steel cleanliness (the level of impurities that the steel have from its birth), alloy addition (Cr, Ni, Mo, Nb, V), microstructure control and carbide distribution, yield to tensile strength ratio, hardness and toughness. Examples of new designed steels are included in Figure 1 for CO_2 corrosion fatigue tests. As can be seen, the performance was on average doubled with the new grade. The same improved performance was observed in H_2S corrosion fatigue tests.

Corrosion in couplings

Field experience on the use of class T couplings suggests that 8630 steels perform better than 4140 steel under corrosive environments. The simplest and common method of measuring corrosion rates is simply to expose a carefully weighed piece of the material to the corrosion environment for a known length of time, remove and reweigh it, and calculate the mass lost. Lab testing using this method has been performed in order to compare the performance of different steels in extreme conditions. First results showed that corrosion rate is at least doubled in 4140 compared with 8630. Considering these results, new steels were designed that showed even better behavior.

The design is based on a reduction of the carbon content, while increasing the alloy addition to maintain the desired mechanical properties.

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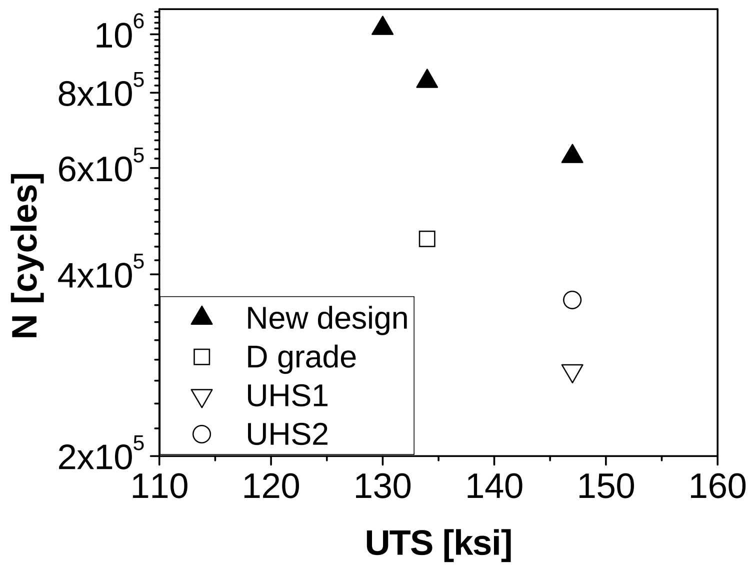

Figure 1 – Corrosion fatigue results under sweet environment. Number of cycles vs. ultimate tensile strength for various steels. Tests performed at 60°C, at 10 bar of CO_2 and a total pressure of 31 bar in a simulated formation water with pH 5.

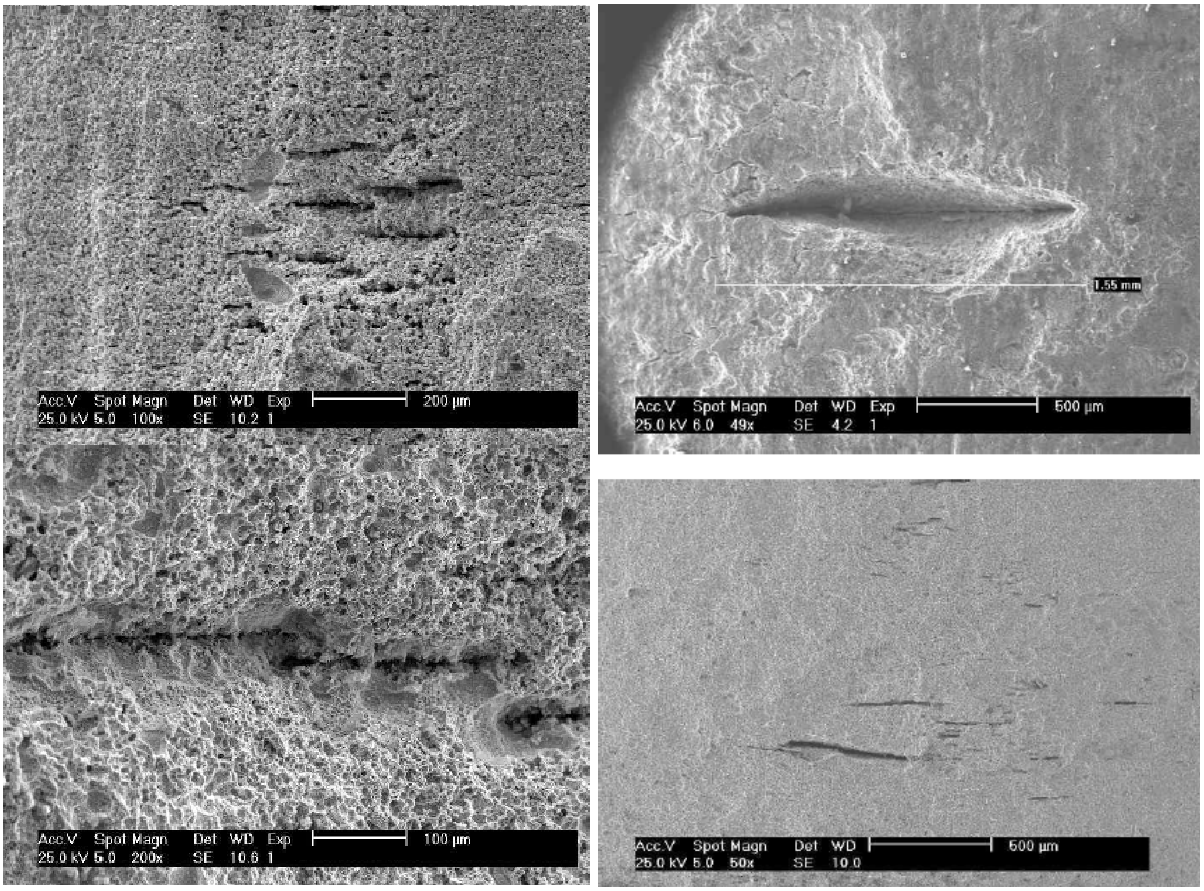

Figure 2 – Morphology of cracks in Lab tests (left) and field failures (right) in the same steel grade, in CO_2 containing environments.