

# Corrosion in the Oil and Gas Industry: An Increasing Challenge for Materials

TERESA E. PEREZ<sup>1,2</sup>

1.—Tenaris, Buenos Aires, Argentina. 2.—e-mail: tperez@tenaris.com

Important reserves of oil and gas, which are left to be discovered and produced, are mainly concentrated in challenging locations and under severe conditions [i.e., high pressure (HP)/high temperature (HT)]. The HP/HT plus the presence of aggressive environments mean a highly demanding scenario for tubes used in producing oil and gas [oil country tubular goods (OCTG)]. Material property requirements include high mechanical properties at ambient and high temperatures (e.g., as high up to 200–250°C). Additionally, if H<sub>2</sub>S is present, resistance to sulfide stress cracking may be required, depending also on other environmental conditions. Even without H<sub>2</sub>S, contents of CO<sub>2</sub>, chlorides, and high temperatures and pressures can represent a risk of high corrosion rates. The improvement of some of the required properties of the materials (e.g., steels) can mean the impairment of other properties. Consequently, a careful balance is required and limits exist for the individual modification of the properties. The present article focuses on the two main environmental deterioration problems in the oil and gas business: (I) sulfide stress cracking and (II) CO<sub>2</sub> corrosion. A description of the acting mechanisms and the effect of environmental and material factors are presented. Selection criteria and current material limitations are also discussed.

## INTRODUCTION

Significant recoverable reserves of oil and gas left to be discovered and produced are mainly concentrated in challenge locations, such as deep-water offshore, remote arctic locations, and difficult-to-manage reservoirs with unconsolidated sands. Additionally, aggressive environments (i.e., high H<sub>2</sub>S and/or CO<sub>2</sub> contents) with high pressures and high temperatures are conditions to be faced by materials in many wells.

Materials and corrosion control technologies to be used under such demanding conditions and locations must be highly reliable due to the excessive cost of replacement or failure in these difficult-to-access locations.

The main concerns for downhole tubulars from the related corrosion problematic point of view are environmental cracking and uniform or localized corrosion.

The total annual cost of corrosion in the oil and gas production industry is estimated to be US\$1,372 billion, broken down into \$589 million in surface

pipeline and facility costs, \$463 million annually in downhole tubing expenses, and another \$320 million in capital expenditures related to corrosion.<sup>1</sup> It is widely recognized within the oil and gas industry that effective management of corrosion will contribute toward not only cost reduction but also compliance with safety, health, and environmental policies.

Even though slightly different definitions for high-pressure, high-temperature (HP/HT) conditions are used, most companies currently categorize their operations, products, or tools into the three main tiers<sup>2</sup> (Fig. 1).

The increment of temperatures and pressures in the wells means that materials with higher mechanical properties, even at the upper range of operation temperatures, are required. Moreover, the aggressiveness of the environment has to be considered.

CO<sub>2</sub> and H<sub>2</sub>S gases in combination with liquid water are the main causes of corrosion in oil and gas production. In addition, it is normal practice to reinject production water downhole to maintain the

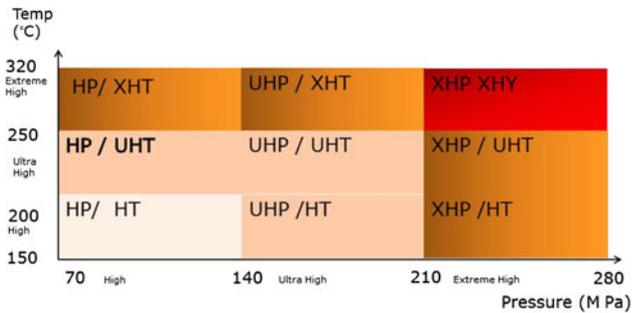


Fig. 1. Matrix of high-pressure/high-temperature operation.

reservoir pressure and stability as well as perform water flooding (using seawater or fresh water sources) to drive oil out of the formation. As a field ages, the ratio of water to oil in the produced fluids increases and can reach levels of 95% or higher. This rise in water content implies an increase in corrosion problems. Internal corrosion caused by produced fluids is the most costly of the corrosion problems in the oil and gas industry since internal mitigation methods cannot be easily maintained and inspected. Therefore, as a field ages, corrosion control becomes more expensive. Approximately 60% of oilfield failures are related to CO<sub>2</sub> corrosion; it can produce not only general corrosion but also localized corrosion, which is a much more serious problem.

Regarding H<sub>2</sub>S, three are the environmental degradation-related phenomena in production and transportation: weight loss corrosion in sour service conditions, localized corrosion (mainly pitting), and sulfide stress cracking (SSC). The SSC risk has been given the highest level of attention because of its dramatic safety impact. Materials, such as carbon steels, can suffer catastrophic failures due to the presence of H<sub>2</sub>S under certain levels of pressure, temperature, pH, and tensile stresses. In fact, crack propagation can take place very fast and produce very serious economic and environmental problems. Due to this fast cracking development, even short and unexpected exposure must be considered during material selection. As MR0175/ISO 15156<sup>3</sup> states, the definition of exposure conditions shall include both intended exposures and unintended exposures that may result from the failure of primary containment or protection methods. This is an important difference in material selection when a corrosion problem is the issue. In this case, it takes longer for damage to occur. Therefore, exposure time can be a criterion to define “acceptable corrosion damage.”

In summary, the material selection must focus first on SSC as the most relevant aspect and the aim must be to avoid any risk of cracking. After that the corrosion risk has to be considered.

Carbon and low-alloy carbon steels (LAS) are the first alternative to be considered in material selection not only from the cost point of view but also due to their availability. Therefore, big efforts have been

made to increase the corrosion resistance of carbon and low-alloy steels. When the environment is too aggressive for bare carbon steels, one option to reduce corrosion problems is the use of inhibitors. However, under highly aggressive environmental conditions and high temperatures, more expensive materials, such as corrosion-resistant alloys (CRAs), may be required.

Another challenging scenario for oil country tubular goods (OCTG) products is related to carbon capture and storage technologies. These technologies are some of the mitigation options to reduce the impact of CO<sub>2</sub> on the global climate. CO<sub>2</sub> can be stored in geological formations, e.g., deep saline formations and depleted oil and gas reservoirs. Existing or new wells can be used for injecting CO<sub>2</sub> into underground storage facilities.

In general, the downhole injection system consists of a casing pipe, a downhole tubing, and a wellhead to prevent blowout. As the underground pressure must be overcome, the system operates at a high pressure to inject the CO<sub>2</sub> into the storage facility.<sup>4</sup> CO<sub>2</sub> is usually injected in a supercritical state.

Depending on the CO<sub>2</sub> source, injected gas composition and water content vary and different contaminants like SO<sub>x</sub>, NO<sub>x</sub>, H<sub>2</sub>S, and/or O<sub>2</sub> can be present. These impurities when present in even moderate amounts have an important effect; they dissolve readily in water and induce the formation of an aqueous phase at a much lower water concentration than the solubility limits reported for pure CO<sub>2</sub> and CO<sub>2</sub> contaminated with hydrocarbons. If liquid water is present with those contaminants in solution, serious corrosion problems can take place.<sup>5,6</sup>

In summary, CO<sub>2</sub> injection wells for sequestration are highly challenging in many ways mainly due to the fluids and pressures they must handle and the long-term duration for which full well integrity is required.<sup>7</sup> The corrosion risk related to the feasibility of having liquid water plus aggressive species in solution has to be considered.

The present article focuses mainly on the environmental deterioration problems in the oil and gas business previously mentioned. A description of acting mechanisms and the effect of environmental and material factors are presented. Selection criteria and current material limitations are also discussed.

## SULFIDE STRESS CRACKING

The first cases of SSC in the oil and gas industry were reported in the tubing and casing of gas wells in the United States and Canada in 1950–1951.

The presence of hydrogen sulfide (H<sub>2</sub>S) is an ever increasing problem in the oilfield, whether the origin is biological or formation dependent. Biogenic formation by the microbial action of sulfate reducing bacteria (SRB) is one of the main reasons for H<sub>2</sub>S progressive concentration increase because SRB

reduce existing sulfate ions to  $H_2S$  gas. One of the most common techniques for enhanced oil recovery is injection water, and nonadequately treated injected water has been a source of bacteria contamination of aquifers.

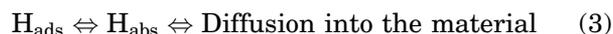
### Hydrogen Embrittlement Mechanisms

It is well known that the presence of atomic hydrogen in solid solution severely degrades the fracture resistance of high-strength metallic alloys (e.g., carbon and low-alloy steels). This process is known as hydrogen embrittlement or hydrogen-induced cracking. The hydrogen deleterious effect has a relevant industrial and economic impact being, at the same time, a challenge from the scientific point of view. Due to the previously mentioned facts, an intensive effort has been done to understand the involved mechanisms and hundreds of papers have been published.<sup>8–14</sup> Despite those efforts, hydrogen embrittlement mechanisms continue to be widely discussed and different theories have been proposed. However, a generally recognized common feature of all the theories that attempt to explain embrittlement in nonhydride former materials is that some critical concentration of hydrogen must be reached at a potential crack site for failure to initiate. In this context, sites in which hydrogen is preferentially accumulated are key points to explaining crack initiation. These sites are called hydrogen traps, and by definition, they have higher binding energy than the lattice and, therefore, they are potential crack initiators.<sup>15,16</sup> According to their binding energy, they can be categorized in irreversible/deep or flat/reversible traps. Binding energy for flat traps is higher than the one for the lattice, but at the same time, hydrogen interchange with the lattice can occur. Although there is no consensus about the role of each trap on embrittlement, traps have been extensively studied, particularly in iron alloys. Some authors<sup>17,18</sup> propose that only *mobile* hydrogen in solution or in a flat trap is involved in fracture. Pressouyre and Bernstein,<sup>19–21</sup> suggest that initiation will be produced at irreversible traps since they can accumulate a large amount of hydrogen and achieve the critical concentration. In their approach, mobile hydrogen only accelerates or retards crack initiation depending on the charging conditions.

Atomic hydrogen can be introduced globally throughout the microstructure by manufacturing operations (e.g., casting, welding, surface-chemical cleaning, electrochemical machining, electroplating, and heat treatment) as well as by environmental exposure (e.g., cathodic electrochemical reactions at low temperatures and gaseous hydrogen exposure at elevated temperatures).

A very simplified description of the mechanism of atomic hydrogen introduction in a material can be presented considering the following steps. Atomic hydrogen is produced by the proton reduction and

its chemiadsorption on the surface ( $H_{ads}$ ) (Eq. 1). This  $H_{ads}$  can be consumed either by H combination (Eq. 2) or by absorption into the bulk of the material (Eq. 3). However, the actual mechanism includes a combination of chemical and electrochemical steps occurring simultaneously.<sup>22,23</sup> Concurrently, the anodic corrosion reaction of the steel takes place on the surface:



The presence of tensile stresses (applied and/or residuals) is recognized as another required factor for hydrogen embrittlement cracking. The effect of stresses on hydrogen solubility was first addressed by Beck et al.<sup>24</sup> in pure iron and in AISI 4340 steel. Different relationships were proposed to express the effect of tensile stresses on solubility.<sup>25–28</sup>

As is schematically shown in Fig. 2, the crack propagates when a critical concentration of atomic hydrogen is reached at a certain point of the material. This threshold depends not only on the material characteristics and the temperature but also on the tensile stress level and the hydrogen concentration itself because they also affect the fracture toughness of the material.

The presence of electronegative species known to poison hydrogenation recombination reactions on transition metals drastically increases the adsorbed atomic hydrogen uptake.<sup>29</sup> In oil and gas applications,  $H_2S$  has the deleterious effect of promoting hydrogen uptake.<sup>30,31</sup> Although many explanations have been proposed to account for these effects, the detailed mechanism of the action of  $H_2S$  is not yet fully understood.<sup>32–35</sup>

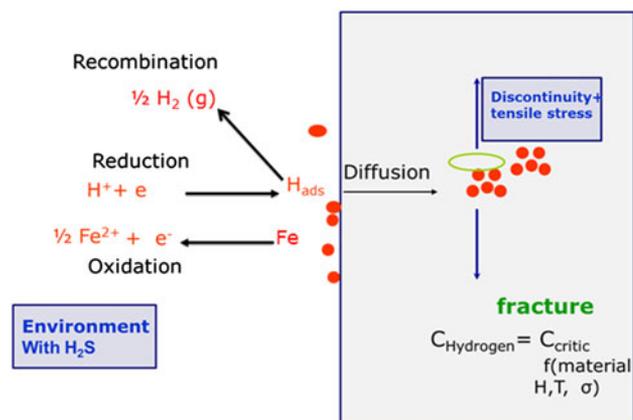


Fig. 2. Schematic representation of SSC mechanism.

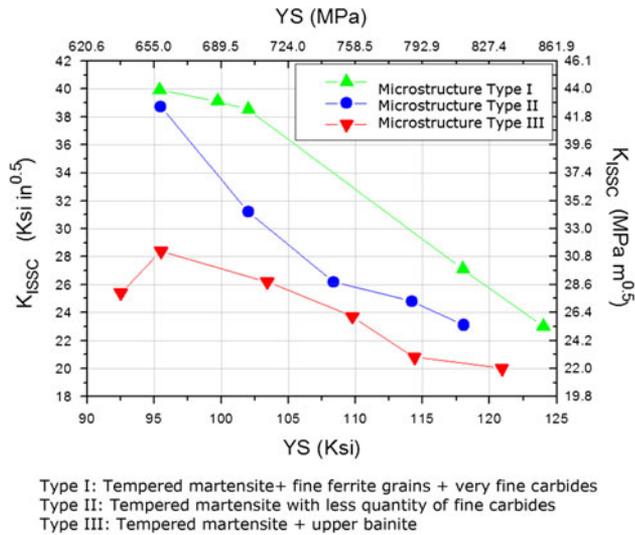


Fig. 3. Effect of mechanical properties and microstructure on cracking resistance of LAS (expressed in terms of a critical stress intensity factor). Test solution A NACE TM0177-2005.<sup>36</sup>

## Development of High-Strength LAS for Sour Service Environment

As previously stated, carbon and low-alloy steels are the first alternative in material selection for oil and gas exploration, drilling, and production. This is particularly applicable for sections that are not continuously in contact with production fluids, but the exposure to the primary aggressive environment is usually accidental and of short duration (for instance, due to a tubing leak). Production casing above the packer is an example of this category. If a sour environment is present, the resistance to SSC has to be ensured. For deep wells, high mechanical properties will be the additional requirements.

As shown in Fig. 3,<sup>36</sup> the H<sub>2</sub>S cracking resistance (expressed in terms of a critical stress intensity factor, KISSC<sup>37</sup>) drastically decreases as the mechanical resistance increases.

Consequently, the development of LAS with high mechanical properties and good resistance to H<sub>2</sub>S cracking is an important and very challenging aim.

The role of the microstructure on SSC resistance was recognized many years ago.<sup>36,38</sup> Quenched and tempered microstructures with low dislocation density and a homogenous and fine distribution of spherical carbides have shown the best performance. Meanwhile, the presence of upper bainite is highly detrimental. Additionally, many publications show a clear relationship between microstructural refinement and SSC resistance.

Steel design and production process conditions have to be defined to get the mentioned desirable microstructural characteristics.

Nb and Ti microalloying additions and controlled rolling conditions are used to avoid excessive grain growth during this process. A double-quenched and

tempered process is sometimes used to get an extra grain size refinement. The austenization temperature prior to quenching must be selected as low as possible to get a fine grain in a consistent way with a full dissolution of iron carbides and complete homogenization of carbon.

The chemical composition plus quenching conditions have to ensure adequate hardenability to avoid undesirable microstructures after quenching even for heavy walls.

Increasing the tempering temperature as much as possible by adjusting the chemical composition (Cr-Mo and microalloying V-Nb) is recommended to get the optimum final microstructure.

The cleanness of the steel is another key factor because inclusions can act as nucleation sites of cracks. Additionally the content of elements such as P and S has to be minimized.

Tensile residual stresses and cold deformation have to be avoided as well. Stress relief requirements are specified in ISO 15156 for materials that are cold deformed after heat treatment.

Applying all of this background together with tight process control conditions for LAS pipes of 110 grades (110 ksi as minimum yield strength) have been developed, and the Grade C110 is currently included in API 5CT.<sup>39</sup> Additionally, proprietary grades with higher mechanical properties (minimum yield strength of 125 ksi) have been developed.

## Selection of Materials Suitable to Be Used in H<sub>2</sub>S-Containing Environments

ISO 15156 gives requirements and recommendations for the selection and qualification of materials for sour environments. Regarding carbon and low alloy steels, ISO 15156-Part 2 presents two different options for the selection:

- Option 1: Only considers the H<sub>2</sub>S partial pressure as the defining parameter. If the partial pressure of H<sub>2</sub>S in the gas is  $\geq 0.3$  kPa (0.05 psi), SSC-resistant steels shall be selected. The application of API 5CT/ISO11960 grades depends on material requirements (i.e., chemical composition, method of manufacture, strength, hardness, heat-treatment condition, and microstructure) and on minimum exposure service temperatures. For proprietary steel grades, in addition to previous requirements, SSC resistance shall be demonstrated by testing each test batch.
- Option 2: Allows the user to qualify and select materials for SSC resistance for specific sour-service applications or for ranges of sour service. In situ pH and H<sub>2</sub>S partial pressure are considered to define regions with different severity (Fig. 4).

The selection can be performed if requirements regarding mechanical properties (which depend on the application region) are filled. Additionally, low-alloy steels may be tested and qualified for use

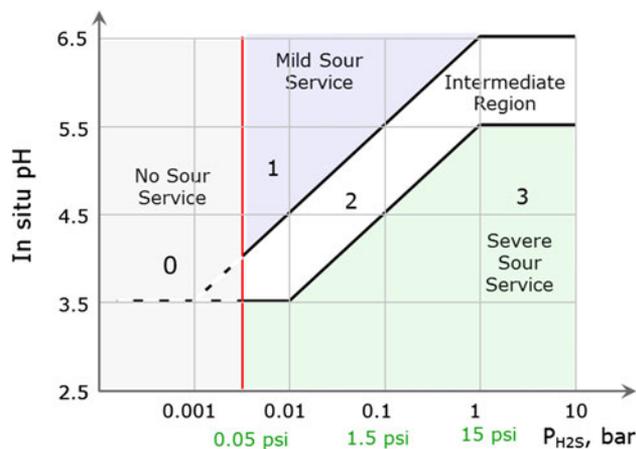


Fig. 4. Regions of environmental severity with respect to the SSC of carbon and low-alloy steels<sup>3</sup>.

under specific sour-service conditions or for use throughout a given SSC region.

The requirements and recommendations for the selection and qualification of CRAs and other alloys for service in equipment used in oil and natural gas production and natural gas treatment plants in H<sub>2</sub>S-containing environments are given in NACE MR0175/ISO 15156-Part 3. The acceptable metallurgical conditions and environmental limits for which CRAs are expected to resist cracking are also provided in Part 3.

## CO<sub>2</sub> CORROSION

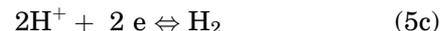
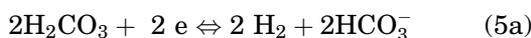
CO<sub>2</sub> or “sweet” corrosion is by far the most prevalent form of corrosion encountered in oil and gas production.<sup>40,41</sup> Early cases of CO<sub>2</sub> corrosion were reported in gas wells located in Texas in the 1940s. Dry CO<sub>2</sub> is noncorrosive to steels and alloys in downhole conditions, but dissolved carbon dioxide in the produced or condensed water can result in very high corrosion rates particularly when a localized attack takes place. Even corrosion resistance alloys have limits in their resistance depending mainly on their chemical composition. The CO<sub>2</sub> corrosion process is complex, and its understanding still requires further work.<sup>42</sup>

### CO<sub>2</sub> Corrosion Mechanisms and Morphologies

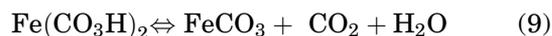
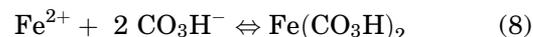
In oil and gas wells, produced fluids could contain significant proportions of CO<sub>2</sub>. Carbon dioxide will dissolve in the aqueous phase associated with hydrocarbon production, forming carbonic acid (Eq. 4):



Three main cathodic (Eqs. 5a–c) reactions and one anodic (Eq. 6) reaction can be identified:



During this corrosion process, iron carbonate FeCO<sub>3</sub> can be formed on the steel surface (according to Eqs. 7–9), if the limit of solubility of FeCO<sub>3</sub> is reached. The solubility depends on the solution pH, CO<sub>2</sub> partial pressure, and temperature.<sup>43–46</sup> This precipitate can act as a protective layer that reduces the uniform corrosion rate of the steel. However, under certain environmental conditions, when the FeCO<sub>3</sub> protective layer is partially destroyed, localized corrosion can take place:



The morphology of the CO<sub>2</sub> corrosion attack can be uniform. Additionally, three main forms of localized corrosion can be identified: pitting (Fig. 5a), mesa attack (Fig. 5b), and flow-induced localized corrosion (Fig. 5c).

Pitting of carbon and low-alloy steels typically takes place at low-flow velocities and around the dew-point temperatures in gas wells. Pitting in oil wells with scaling tendency has also been observed. The pitting tendency increases with temperature and CO<sub>2</sub> partial pressure. The actual mechanisms of pitting of carbon steels in CO<sub>2</sub> environments are not clear, and there are no rules for its prediction.

Mesa attack is associated with low-to-medium flow, where a protective carbonate film is formed but it is unstable. Bare areas act as an anode of a galvanic cell where surrounding film-covered areas operate as the cathode.

Flow-induced corrosion is related to high-flow velocities and turbulence. Pits, mesa attack zones, or particular geometries can produce local turbulence. Turbulence, in turn, may destroy existing protective scales and prevent reformation on the exposed metal.

### Factors that Determine the Severity of CO<sub>2</sub> Corrosion of Carbon and Low-Alloy Steels

The actual morphology of the corrosion, as well as the corrosion rate, will depend mainly on the formation of a protective layer of corrosion products, its effective adherence, and its capability of reforming in case of local damage. Consequently, the severity

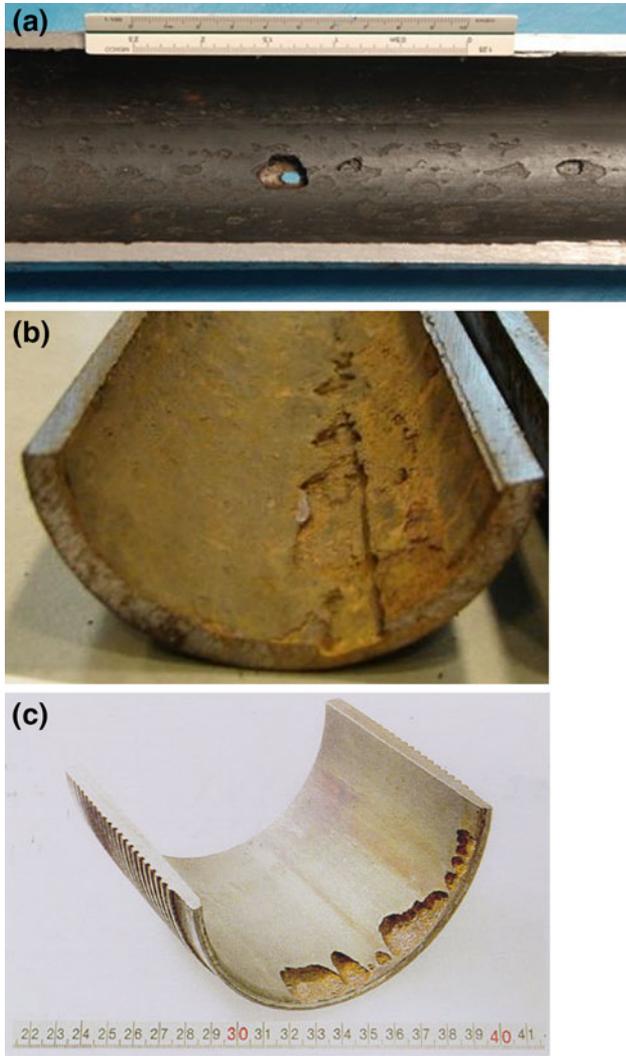


Fig. 5. (a) Pitting attack. (b) Mesa attack. (c) Flow-induced localized attack.

of carbon dioxide corrosion of carbon and low-alloy steels will be influenced by all those factors that can affect the corrosion layer formation and properties. The following environmental parameters will have a interactive effect:

- CO<sub>2</sub> partial pressure
- Temperature
- Water content (water cut) and water chemistry
- pH
- Flow velocity and type
- Presence of H<sub>2</sub>S, oxygen, and organic acids

The corrosion severity increases for high CO<sub>2</sub> partial pressure, flow velocity, water content, and low pH. The effect of CO<sub>2</sub> partial pressure and temperature on the corrosion rate of low-alloyed carbon steel is presented in Fig. 6. Temperature affects the nature and characteristics of the corrosion product, which influence corrosion. The

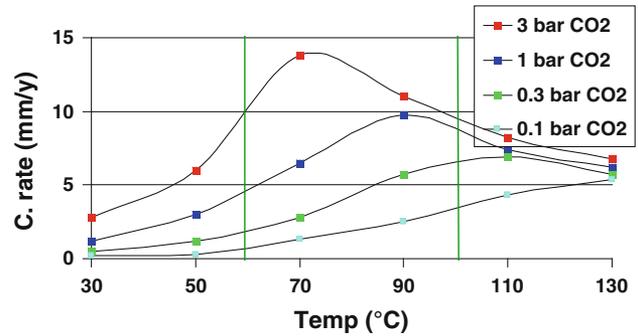


Fig. 6. Effect of temperature and CO<sub>2</sub> partial pressure on the corrosion rate of a LAS.

uniform corrosion rate tends to present a maximum at a certain temperature (around 60–100°C) depending on the other environmental conditions (e.g., CO<sub>2</sub> partial pressure and pH).

Organic acids are short-chain carboxylic acids, mainly acetic acid (C2) but also some propionic and butyric acids (C3 and C4). They are usually produced with the hydrocarbon in both gas and oil production wells. They strongly influence CO<sub>2</sub> corrosion process and hence affect corrosivity assessment and predictions.

When organic acids are present, the corrosion problems can appear at considerably lower CO<sub>2</sub> partial pressures.<sup>47–52</sup> Their effect and the acting mechanisms are still under discussion.

In condensed water, the free acetic acid content (HAc) is physically dissolved from the gas (or oil) phase, and this induces an over acidification of the CO<sub>2</sub> solution. When HAc becomes the dominant acid, it increases the solubility of the corrosion products, which means increasing the iron content (Fe<sub>sat</sub>) at the saturation of the corrosion products (FeCO<sub>3</sub>). Relative quantities of HAc and CO<sub>2</sub> will determine which one is the acting acid. For gas fields, empirical thresholds have been proposed (Table I).

The values reported in Table I are only estimations. The real mechanisms are not completely understood and the different parameters have strong interactions between them.

Crolet et al.<sup>53</sup> tried to identify what might differentiate fields with and without organic acids with respect to the currently understood mechanisms of CO<sub>2</sub>, and to explain the reported threshold values. They showed that empirical field thresholds of 1 mM and 0.1 mM HAc actually correspond to the same acidifying power as 2 bar and 0.2 bar of pure CO<sub>2</sub>, e.g., nearly the API limits of the 1958 limit values for CO<sub>2</sub> (<0.2 bar low corrosiveness; >2 bar high corrosiveness).

In reservoir water, the free HAc is chemically produced from the total acetate content (Ac<sub>tot</sub>) and the dissolved CO<sub>2</sub>, and this does not practically change anything on the Fe<sub>sat</sub>. It just occurs that in strongly buffered waters, the HAc value in mM is always close to that of Fe<sub>sat</sub> in ppm, so that the free

**Table I. Proposed empirical thresholds for acetic acid in gas wells**

| Free HAC (meq/L) | Dominating acid                           | Corrosion process governed by                 |
|------------------|---|---|
| <0.1             | CO <sub>2</sub> becomes the dominant acid | CO <sub>2</sub> corrosion                     |
| 0.1–1            | Mixed dominance of both acids             | Mixed corrosion                               |
| >1               | Essentially HAC                           | HAC corrosion. Independent of CO <sub>2</sub> |

HAc is not too bad a marker of the solubility of the corrosion products. Thresholds of HAC are then low because the corrosion layers can be sufficiently protective only at low Fe<sub>sat</sub>.<sup>53</sup>

The effect of the microstructure of LAS on CO<sub>2</sub> corrosion has been widely studied, but many issues are still uncertain and contradictory results can be found in the literature.<sup>54–59</sup>

Regarding the effect of steel composition, the positive influence of low Cr additions (~3%) on CO<sub>2</sub> corrosion performance of standard carbon steel is reported in the literature.<sup>60,61</sup> Energy-dispersive x-ray and Fourier transform infrared analysis showed that chromium-enriched surface films (iron/chromium oxy-hydroxides) are formed during the corrosion process causing a corrosion rate reduction. A new generation of low-carbon 3%Cr microalloyed steels has been developed as an intermediate option for well completions in terms of corrosion resistance and economy.<sup>62,63</sup> The material showed good performance in mature oil wells, with high water cut (even >90%), high chloride content (in cases higher than 150,000 mg/L), and moderate CO<sub>2</sub> partial pressure moderate (up to 1 bar or slightly higher).<sup>64,65</sup>

### Effect of H<sub>2</sub>S on CO<sub>2</sub> Corrosion: Limits Between Sweet and Sour Corrosion

The presence of small concentrations of H<sub>2</sub>S can have a significant effect on CO<sub>2</sub> corrosion; this is because iron sulfide can precipitate as the corrosion product in CO<sub>2</sub>/H<sub>2</sub>S environments. Depending on the exposure conditions, different forms of FeS can form (Fig. 7),<sup>66</sup> and their specific corrosion protectiveness may be different. A significant amount of information is reported in the literature regarding the formation of the various FeS species as well as the impact that each has on further corrosion. However, there is still a great deal that is not known. For example, there are currently no generally accepted prediction algorithms for any form of H<sub>2</sub>S corrosion. There are also still a number of unknowns about the corrosion reactions that lead to pitting, which is the most common mode of sour service equipment failure.<sup>67</sup>

To determine how much H<sub>2</sub>S is required to turn a system from sweet to sour corrosion, different rules of thumb have been used. In the 1980s, Dunlop et al.<sup>68</sup> proposed the use of a CO<sub>2</sub>/H<sub>2</sub>S ratio of 500 at 25°C to determine whether the corrosion product will be FeCO<sub>3</sub> or FeS. For values >500, the product will be FeCO<sub>3</sub> and <500 the product will be FeS. Other authors proposed a ratio of CO<sub>2</sub>/H<sub>2</sub>S lower

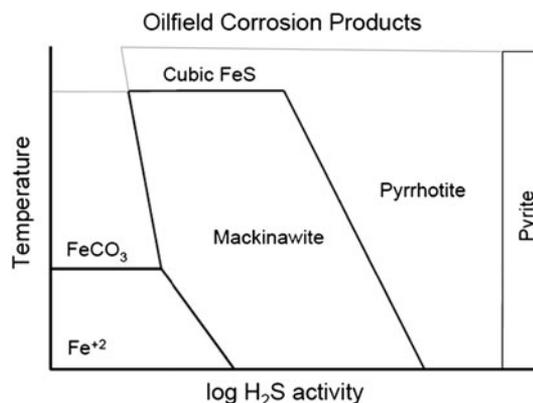


Fig. 7. Corrosion product formation as a function of temperature and H<sub>2</sub>S.<sup>66</sup>

than 20 to have sour corrosion, while a mixed regime is considered when the ratio ranges between 20 and 500 and sweet corrosion for values higher than 500.

The ratio of 500 for the CO<sub>2</sub>/H<sub>2</sub>S is referenced in a number of industry documents.<sup>69,70</sup> However, some authors<sup>71</sup> consider that the use of the CO<sub>2</sub>/H<sub>2</sub>S ratio as a rule of thumb to determine sweet versus sour corrosion conditions is not recommended because the effective ratio is too sensitive to thermodynamic input data quality to be a useful engineering tool. Existing computer tools that model corrosion chemistry and can calculate FeCO<sub>3</sub> and FeS formation should be used instead.

A review of a wide number of field cases<sup>72,73</sup> reports quantitative information about sour weight loss corrosion and proposes possible mechanisms. The fluid corrosiveness is classified into three categories, from a negligible corrosiveness in 40%–50% of the cases (both in oil and gas production), to a moderate one (typically within 1 mm/year) in most of other cases, and lastly to a very severe corrosion (10 mm/year, even in apparently mild conditions) in a few cases. The flow velocity and flow regime are shown to be the most leading factors of the transition between negligible and intermediate and severe corrosion categories. Very severe corrosion cases require “pit promoters” (sulfur, oxygen, and bacteria) and a “galvanic effect” with surrounding non-corroding surfaces. On the other hand, the H<sub>2</sub>S and CO<sub>2</sub> partial pressure as well as the pH or the H<sub>2</sub>S/CO<sub>2</sub> ratio does not influence the corrosion likelihood if the CO<sub>2</sub>/H<sub>2</sub>S ratio is lower than 20.

Other references<sup>74</sup> also report that sour oil wells are never corrosive at least above 3% H<sub>2</sub>S in the acid–gas mixture. The same is true for gas wells with an active aquifer, i.e., producing their reservoir water in the same way as oil wells. Conversely, the bottomhole of HP gas wells above 450 bars with no active aquifer will sooner or later pass through a corrosive period, due to the presence of trapped water slugs, whereas the condensing zone at the top will never be corrosive.

### Prediction of Corrosion Rate and Material Selection

An industry standard approach for predicting CO<sub>2</sub> corrosion does not exist. There are no standards or guidelines like there are for H<sub>2</sub>S cracking (e.g., ISO 15156).

Different relationships between environmental variables and tendency to sweet corrosion have been proposed. They range from the simplest “rules of thumb” based on CO<sub>2</sub> partial pressure<sup>75</sup> to complex predicting models.

Oil companies and research institutions have developed a large number of CO<sub>2</sub> corrosion predicting models.<sup>76–85</sup> Several models are mainly based on empirical correlations with laboratory data, while others are partly based on field data. In addition, some other models are based on mechanistic approaches of the different chemical and transport reactions. In 2010, an overview of different prediction models used in the oil and gas industry for evaluation of CO<sub>2</sub> corrosion of carbon steel was presented.<sup>86</sup> Models differ considerably in how they predict the effect of protective corrosion films and the effect of oil wetting on CO<sub>2</sub> corrosion, and these two factors account for the most pronounced differences between models.<sup>86</sup>

Additionally, a set of the most used models were evaluated against field data. Depending on the field cases, different models were most successful in their prediction, and it was not possible to identify one or two models as better than others.<sup>87</sup>

Using the CORMED software for the quantitative assessment of the protectiveness leading parameters, Crolet et al.<sup>88</sup> concluded that in any well producing reservoir water, only a sufficient presence of free HAc and the solubility of iron acetate can

jeopardize the protectiveness of FeCO<sub>3</sub> layers. In wells producing condensed water, only the very low pH values associated with high P<sub>CO<sub>2</sub></sub> figures can also jeopardize this protectiveness. Based on their algorithms, new prediction rules for downhole CO<sub>2</sub> corrosion were proposed (Table II).

When selecting CRAs, environmental conditions that can affect its passive layer and cause localized corrosion have to be considered (i.e., chlorides, temperature, disrupted flow, and presence of sand). Additionally, process factors (i.e., mechanical damage by wire line operations and acidification) can also damage the passive layer and promote localized corrosion. For CRAs, the worst conditions for general and localized corrosion are normally associated with the maximum service temperature. Prediction models are not common for CRAs, and typically, application domains<sup>89</sup> and even rules of thumb are used during their selection.

### SUMMARY: WHAT ARE THE CHALLENGES FOR THE FUTURE?

High-pressure/high-temperature applications are pushing the limits of materials for oil and gas exploration and production technology. HP/HT plus the presence of aggressive environments mean a highly challenging scenario for OCTG. Under these conditions, requirements for pipes will include not only characteristics related to material properties but also connection properties and geometry tolerances to fulfill the well design requisites.

Material property requirements include high mechanical properties at ambient and at high temperatures (e.g., as high as 200–250°C). Additionally, if H<sub>2</sub>S is present in the environment, resistance to SSC may be required, depending also on the other environmental conditions. Even without H<sub>2</sub>S, contents of CO<sub>2</sub>, chlorides, and high temperatures and pressures can represent a risk of a high corrosion rate.

As discussed, the improvement of some of the required properties of steels can mean the impairment of others. Consequently, a careful balance is required and limits exist for the individual modification of the properties.

In light of this scenario, the following questions appear on our horizon:

1. What is the improvement level that can be achieved for properties of the currently used materials through the enhancement of material design and process conditions? In other words, how far from their limits regarding key properties are the currently used materials?
2. Which are the alternative new materials (e.g., nanomaterials) for the industry? Are there new options of bulk materials and/or surface treatments on more conventional materials?
3. Are new material technologies able to generate materials that represent a breakthrough with a quantitate jump in properties?

**Table II. Prediction rules for downhole CO<sub>2</sub> corrosion<sup>86</sup>**

| Expected corrosion | P <sub>CO<sub>2</sub></sub> max (bar) |     | in situ HAc (mM) |
|--------------------|---------------------------------------|-----|------------------|
| Condensed water    |                                       |     |                  |
| Low/acceptable     | <5                                    | and | <1               |
| High/unacceptable  | >5                                    | or  | >1               |
| Reservoir water    |                                       |     |                  |
| Low/acceptable     | –                                     |     | <0.1             |
| High/unacceptable  | –                                     |     | >0.1             |

Even after getting positive answers for our last questions at a laboratory scale, important challenges remain. After achieving promising results with new technology materials in laboratory conditions, industrial scale implementation is still a challenge. Aspects such as the production of low-cost and easily industrialized materials need to be managed.

The joint effort of the R&D community together with pipe producers and the oil and gas exploration and production industry will be necessary to face these challenges.

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