

Effect of Carbon Dioxide and Hydrogen Sulfide on the Localized Corrosion of Carbon Steels and Corrosion Resistant Alloys

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ABSTRACT

Carbon steels, low alloy steels (LAS) and corrosion resistant alloys (CRA) used in the upstream oil and gas industry may be susceptible to localized corrosion. Several variables control the occurrence of localized corrosion, including alloy composition, heat treatment, and environmental effects such as temperature, and concentration of chloride, oxygen and other species. Regarding carbon and LAS, it is recognized that even small concentrations of hydrogen sulfide (H₂S) can have an important effect on general corrosion rate when compared to environments where carbon dioxide (CO₂) controlled the corrosion phenomenon. However, there are still several unknowns about the effect of H₂S on pitting, which is the most common mode of sour service failure. Regarding CRA, there is contradictory information on the effect of H₂S and CO₂ in the environment and how it affects pitting corrosion initiation and propagation. The purpose of this review is to discuss the environmental effects, especially H₂S and CO₂ on pitting susceptibility of LAS and CRAs.

Keywords: low alloy steels, corrosion resistant alloys, localized corrosion, hydrogen sulfide, carbon dioxide, passivation, PRE, chloride, temperature

CARBON AND LOW ALLOY STEELS

It is well known that pitting and crevice corrosion are a potential risk for corrosion resistance alloys (CRAs). As it will be discussed in the next topic, the local damage of the passive layer is the initiation step for this type of attack. Carbon steels (CS) do not present a passive layer in oil and gas environments; nevertheless, pits can be generated through a different mechanism. Due to the absence of a passive layer, some authors call the pitting in CS "non-classical pitting corrosion".¹

Depending on environmental conditions (temperature, CO₂ and H₂S partial pressures, pH, and water chemistry) protective or partially protective corrosion products can be formed on carbon steels. This is the case of iron carbonate in CO₂ rich environments or iron sulfide corrosion products in sour environments.² Under certain environmental conditions, pitting formation can take place when the protective corrosion layers are locally damaged.

The steps for pitting or other localized corrosion to be produced in a CS are:

- 1- Initially, CS undergoes uniform corrosion.
- 2- Depending on environmental conditions iron carbonate or some iron sulfide can form a protective corrosion product layer. The types, morphology and kinetics of layer formation depend on several operating variables as well.
- 3- Localized attack can take place after the protective layer formation. Generally, the failures are more frequent during the first years of operation^{3,4}

Protective Corrosion Layer Formation

The formation of a protective corrosion layer on a carbon steel can improve their performance under certain environmental conditions. However, the risk of different types of localized attack can appear as well. Iron carbonate is the corrosion protective layer that can be formed in CO₂ corrosion environments; it is often reported as a protective layer if the morphology of iron carbonate is dense and the layer is adherent to the steel.⁵ Due to the key role of iron carbonate on the performance of CS, its formation mechanisms as well as the effect of environmental parameters on the types of iron carbonate have been extensively studied, mainly in the 1990's.^{6,7,8,9,10,11,12}

The FeCO₃ is formed if the product of the ferrous ions concentration and the carbonate ion concentration exceeds the solubility product of FeCO₃. The solubility of the FeCO₃ decreases as the temperature increases. The temperature above which the precipitation takes places depends on the CO₂ partial pressure and the pH. The increment of the CO₂ partial pressure and the pH enhance the precipitation of FeCO₃. The rate of precipitation is relatively slow and allows much higher ferrous ion concentration than the value dictated by the thermodynamic (supersaturation) equilibrium. The supersaturation and temperature are the most important factors affecting the rate of precipitation and the nature and protectiveness of the iron carbonate film.^{13,14,15} Under high flow velocity it is more difficult to reach the saturation level at the steel surface and, consequently, it is more difficult to form a protective layer. Additionally, the flow can damage the protective layer producing localized corrosion if the saturation of the solution is not reached to reform the layer.

Hunnik et al. developed an equation for iron carbonate kinetics. Their main objective was to establish the conditions under which stable protective corrosion product layers form. A good indicator for the formation was the scaling tendency, defined as the ratio between the precipitation and the corrosion fluxes. To form reliable scales, the bulk scaling tendency should be high enough for protective film formation and the local scaling tendency, in case of film damage, should be high enough for film repair. They modeled both processes and found that above approx. 80°C reliable scales often formed easily whereas below this temperature pH values of at least 6.0 were required.¹³

Even the NaCl is the most abundant salt in formation water, other salts (s CaCl₂, MgCl₂, CaCO₃), are also present. Depending on calcium concentration, the formation of mixed carbonates (as Fe_xCa_{1-x}CO₃) can take place.¹⁶ Several authors studied the effect of Ca²⁺ on the formation and protectiveness FeCO₃ layers in aqueous CO₂ corrosion of mild steel. They showed that the isostructurality of calcium carbonate (CaCO₃) and FeCO₃ allowed the incorporation of Ca²⁺ into

the FeCO_3 structure; thus, the morphology and chemical properties of FeCO_3 were altered.^{17,18} Esmaeely et al. studied the effect of Ca^{2+} on the CO_2 corrosion of mild steel in simulated saline aquifer environments (1 wt. % NaCl, 80°C, pH 6.6) with different concentrations of Ca^{2+} (10, 100, 1,000 and 10,000 ppm). Their results showed that with low concentrations of Ca^{2+} (10 and 100 ppm), the corrosion rate decreased with time due to the formation of protective FeCO_3 and/or $\text{Fe}_x\text{Ca}_y\text{CO}_3$ ($x + y = 1$). However, the presence of high concentrations of Ca^{2+} (1,000 and 10,000 ppm) resulted in the change of corrosion product from protective FeCO_3 to non-protective CaCO_3 , and an increasing corrosion rate with time. While the general corrosion rate was high for both 1,000 and 10,000 ppm Ca^{2+} , surface analysis data revealed a different steel surface morphology with pitting observed in the presence of 10,000 ppm Ca^{2+} .¹⁹

The presence of small concentrations of H_2S can have a significant effect on CO_2 corrosion; this is because iron sulfide can precipitate as corrosion product in $\text{CO}_2/\text{H}_2\text{S}$ environments. To determine how much H_2S is required to turn a system from sweet to sour corrosion, different rules of thumb have been used. In the eighties, Dunlop et al. proposed the use of a $\text{CO}_2/\text{H}_2\text{S}$ ratio of 500 at 25°C to determine whether the corrosion product would be FeCO_3 or FeS . For values greater than 500, the product would be FeCO_3 and for less than 500 the product would be FeS .²⁰ Other authors proposed a ratio of $\text{CO}_2/\text{H}_2\text{S}$ lower than 20 to have sour corrosion, while a mixed regime was considered when the ratio ranged between 20 and 500 and sweet corrosion for values higher than 500. The ratio of 500 for the $\text{CO}_2/\text{H}_2\text{S}$ is referenced in a number of industry documents.^{21,22} However, some authors considered that the use of the $\text{CO}_2/\text{H}_2\text{S}$ ratio as a rule-of-thumb to determine sweet versus sour corrosion conditions is not recommended because the effective ratio was too sensitive to thermodynamic input data quality to be a useful engineering tool. Existing computer tools that model corrosion chemistry and can calculate FeCO_3 and FeS formation should be used instead.²³

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 upon 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_2S corrosion. There are also still several unknowns about the corrosion reactions that lead to pitting, which is the most common mode of sour service equipment failure.²⁴ The effect of H_2S on corrosion in oil and gas production has been investigated for a long time. During the 70's and 80's the focus was on souring in the primary production where pyrrhotite was formed due to the high H_2S concentrations and temperatures exceeding 100°C. However, in the last decade the souring of formerly sweet fields due to secondary recovery, put the attention on low H_2S concentrations and lower temperature ranges that produce mackinawite as corrosion products.²⁵ The forms of iron sulfide formed as well as the involved mechanisms will be different for moderate H_2S systems than for slightly sour environments. Depending upon the exposure conditions different forms of FeS can form and their specific corrosion protectiveness may be different.²⁶ Figure 1 illustrates the dependence of temperature and H_2S partial pressure upon the stability of mackinawite and the transition to pyrrhotite.^{15, 27}

The mackinawite upper temperature stability limit is subject to some degree of uncertainty. Taylor calculated an upper limit of 130°C.²⁸ Takeno et al. found a range between 170 and 200°C for the transformation of mackinawite; meanwhile Clark stated the limit is 135°C.^{29,30} There is also an H_2S limit to the mackinawite stability region; beyond this limit, pyrrhotite becomes the corrosion product. In both regions and possibly at higher temperature, kinetics will sometimes allow formation of cubic FeS during short term exposures. Cubic FeS is a thermodynamically metastable phase. Where cubic FeS forms, it will normally transform over a period of a few days into either mackinawite at lower temperatures or pyrrhotite at higher temperatures. A more neu-

tral pH increases the stability region of mackinawite to higher level H₂S at lower temperatures. A more acidic pH would reduce the mackinawite region.¹⁵

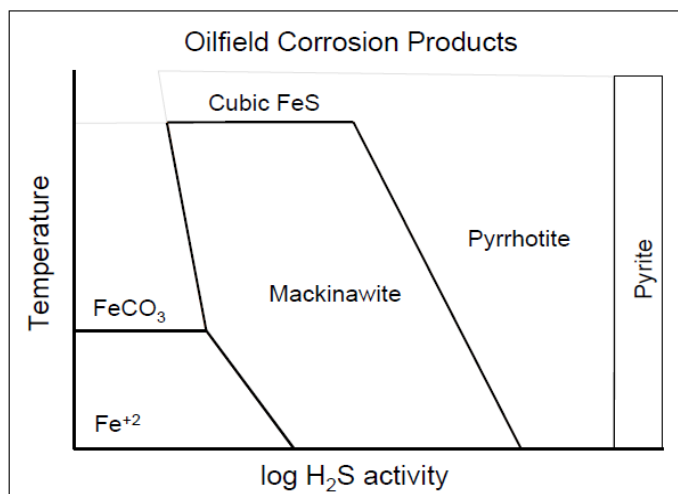


Figure 1: Corrosion Product Formation as Function of Temperature and H₂S¹⁸

It was reported that the iron sulfide formation rate does not significantly depend on the dissolved Fe²⁺ concentration, in H₂S corrosion of mild steels. This is in sharp contrast with CO₂ corrosion where the iron carbonate formation is a function of iron supersaturation, which is the driving force for the FeCO₃ precipitation. Taking this fact into account, several authors provided data that indicated that a direct reaction between the H₂S and the steel surface took place.^{17,31,32} Sun et al. stated that the corrosion mechanism at temperatures below 135°C but above the H₂S partial pressure range where mackinawite was the preferential corrosion product may be at least a two-step process. Regardless of the concentration of H₂S present in the environment, the kinetics dictate that a clean steel surface that is exposed to an environment containing H₂S will form a mackinawite film first if the thermodynamics allow the formation of iron sulfide. Mackinawite formation kinetics is very rapid and the formation of the other forms of iron sulfide are sluggish by comparison. The thickness of the mackinawite film will increase as long as the FeS dissolution rate is lower than the formation rate. The mackinawite growth rate depends upon the environmental conditions such as dissolved H₂S concentration pH and temperature.²¹ When the precipitation rate exceeds the dissolution rate the film begins to grow. During this growing process stresses within the film can produce ruptures. Sun et al. considered that these ruptures are pathways that allow the solution to the metal and continue the corrosion process.²¹ Mackinawite first forms on the metal surface by a solid-state reaction; then the mackinawite layer is overlaid by other phases once they have been given the opportunity to nucleate.^{16, 33} As Smith et al. remarked in their update regarding sour corrosion products studies, that notable progress was obtained to understand the FeS formation under environmental condition where mackinawite is the primary corrosion product. However, more information is required to define the temperatures, partial pressure of H₂S, pH and time conditions that determine whether the outer surface of an iron sulfide will be mackinawite, pyrrhotite or other iron sulfides (FeS).³⁴

Localized Corrosion in Sweet Environments

Pitting, mesa attack and flow induced are the main forms of localized attack found in sweet environments. The localized corrosion is stabilized by system related local differences in electrochemical potential and environment. Important for the corrosion rate at the local anode (e.g. in the pit or at the site of flow induced localized corrosion (FILC)) are the kinetics of the cathodic reactions and the surface ratio between the local cathode and anode. The electronic conductivity of the corrosion product layers is decisive for the mechanism of localized corrosion.³⁵ Regarding the electrochemical mechanism of localized corrosion attack during CO₂ corrosion, some authors assumed that the carbide network could exert a cathodic activity.³⁶ However Schmitt et al. measured the conductivity of iron carbonate and concluded that it is too low to consider as site of cathodic reactions. They stated that both anodic and cathodic reaction must take place on the active surface at the site of localized attack.³⁵

Pitting occurs at low velocities and around the dew-point temperatures in gas wells. The pitting susceptibility increases with the temperature and the CO₂ partial pressure. Chloride content was reported as important in the onset of localized corrosion since it largely affects the ionic strength and the super saturation level of the solution.^{37,38} Different authors remarked the probabilistic character of localized attack and proposed a stochastic approach.^{14,39,40} Even though pitting corrosion of carbon steels in sweet environments has received attention and plenty studies have been developed, the initiation and propagation mechanisms are far to be completely clarified.

In mesa attack, large areas without protective corrosion films, with deep and flat bottom and very sharp edges are developed. The local corrosion rate can reach several mm/years while the surrounded protected areas present very low corrosion. It has long been reported that the mesa attack is flow dependent. Different theories have been proposed to explain how mesa attack develops. One theory considers that intrinsic stress caused by a volume mismatch between the corrosion products and the metals it replaces can break up the corrosion product films. After performing measurements of fracture stresses of iron carbonate scales, Schmitt et al. concluded that hydrodynamic forces expressed in terms of wall shear stresses are orders of magnitude too small to cause destruction of the scales from CO₂ corrosion of carbon steels and initiate FILC. They stated that scales crack and spall after reaching a critical thickness and due to the intrinsic growth stresses.³⁵

Nyborg and Dugstad proposed that the process starts as several small pits growing beneath a porous corrosion film. The corrosion film is removed stepwise by the mechanical forces of the turbulent flow after the metal beneath has dissolved by corrosion. Several pits are initiated in a short period and grow together into a wide mesa attack. The mesa continues growing with high corrosion rate laterally and in depth as long as the protective films are not reformed. A galvanic cell can be set up between the film free region and the covered metal. For this mechanism, the effect of flow on mesa attack is first to remove the thin lid of corrosion film after the steel beneath has corroded away and then to prevent the reformation of protective films.^{41,42}

Yang also studied the removal mechanisms of protective iron carbonate layers and concluded that the layer cannot be removed by hydrodynamic forces of the flow alone and that chemical dissolution of the layer may lead to the exposure of the steel substrate.⁵ Recently, Esmaeely et al. showed that in electrolytes containing high Ca²⁺ concentrations, inhomogeneous corrosion products with composition Fe_xCa_yCO₃ (x+y=1) were formed. In stagnant conditions localized corrosion was observed for high Ca²⁺ contents and Ca²⁺ was responsible for initiation of localized corrosion rather than Cl⁻. The corrosion attack became uniform when flow was introduced.

When the mole fraction of Ca^{2+} in the $\text{Ca}_x \text{Fe}_y \text{CO}_3$ unit cell was close to one the protectiveness of the layer was degraded.⁴³

Localized Corrosion in Sour Environments:

Many references, mainly concerned with high levels of H_2S and elemental sulfur presence, reported pitting as the typical corrosion attack. However, oil and gas fields with high H_2S without pitting are also reported. This could indicate that other factors such as O_2 , chlorides and CO_2 can have a role increasing the likelihood of localized attack in sour environments.^{44,45} Other authors also reported severe pitting corrosion in carbon steels in production field failures of both, wells and pipelines when very high concentrations of H_2S and chlorides are present.⁴⁶ That means that in service conditions where the protective iron sulfide scale can be damaged or it is locally disturbed are present. The main disturbers are chlorides and free elemental sulfur.⁴⁷ A review of a wide number of field cases on quantitative information about Sour Weight Loss Corrosion (SWLC) report severe corrosion cases which require "pit promoters" (sulfur, oxygen, bacteria) and a "galvanic effect" with surrounding non-corroding surfaces.^{48,49}

Kvarekval et al. reported an increment of the local corrosion rate when simulation formation water (100 g/L NaCl) was the testing environment. It was suggested that the chlorides may prevent adhesion of corrosion films to the metal surfaces and lead to the formation of pores in the film. The galvanic effect of conductive deposits such as FeS is also enhanced by the solution conductivity provided by high ionic strength.⁵⁰ From the standpoint of iron sulfide corrosion products, a very special situation exists when a sweet production environment with FeCO_3 corrosion product and the production undergoes souring or where new production is added that is sufficiently sour to change from iron carbonate to an iron sulfide. There is also a chance that some of the FeCO_3 will convert from siderite to FeS.²⁹

Slightly sour systems require careful monitoring, because even the corrosion rate is dominated by CO_2 , FeS can also be formed. As it is cathodic to the steel, it can produce pitting with very high local corrosion rates. Higher H_2S levels result in stable scales and reduction of the corrosion rate as long as the sulfide layer can be maintained.²² Because mackinawite is an electron conductor the cathodic reaction may occur on the surface of the mackinawite with the anodic sites in the bare metal. The higher corrosion potential difference between sour scale and steel causes greater pitting tendency in sour corrosion compared to sweet corrosion.⁵¹ Tjeita et al. studied the effect of galvanic coupling between different iron sulfides (troilite, pyrrhotite and pyrite) and steel electrode. The result shows that all the iron sulfides act as cathodes, with pyrrhotite having the highest effect. Consequently, if the iron film is locally damaged, the cathode to anode ratio may become very large, resulting in large localized corrosion rates.⁵² As Smith pointed out, since 2006, the understanding of mackinawite formation has made significant advancements; however, more studies are necessary under conditions where pyrrhotite is formed. They remark that the film rupture mechanisms and consequences of these ruptures need to be studied to understand if localized corrosion of the steel beneath the ruptures can take place.³⁰

Pitting is the consequence of a complex combination of factors; the synergistic effect of all these factors is not fully understood and no rules for pitting prediction are available.

CORROSION RESISTANT ALLOYS

NACE International Publication 1F192 (2013 Edition) defines CRA as an “alloy with an inherently low corrosion rate in the operating environment of interest, typically much lower than carbon and low-alloy steels (e.g., 1 to 2 orders of magnitude less).”⁵³ NACE MR0175/ISO 15156-1,¹ Paragraph 3.6 defines corrosion-resistant alloy (CRA) as an “alloy intended to be resistant to general and localized corrosion of oilfield environments that are corrosive to carbon steel.”⁵⁴ The use of CRA is also discussed in the European Federation of Corrosion Publication 17. CRA would be used in the upstream oil and gas environment when the use of carbon steel is not economical due to the presence of either carbon dioxide (CO₂) or hydrogen sulfide (H₂S).⁵⁵ To justify the additional initial cost of using CRA, these should be resistant to general corrosion, localized corrosion and environmentally assisted cracking in the in-situ application. The use of CRA would also reduce the field cost of inspection and monitoring.

Our current manuscript deals with the issue of localized corrosion only, such as pitting corrosion and crevice corrosion. Per NACE definitions, CRAs comprise a large family of alloys including ferritic, martensitic, austenitic and duplex stainless steels, as well as nickel and cobalt alloys and other alloys such as aluminum, brass, zirconium, and titanium (Annex A in Reference 52) (Table 1 – from Table D.1 in Reference 53).⁵³ Some of the alloys listed in NACE MR0175/ISO15156-3 can be ranked by their Pitting Resistance Equivalent (PRE) number, which is defined in Equation 1, where the elements symbols represent the mass of the element in the alloy.⁵⁶ Equation 1 is generally applied to all types of alloys containing chromium for corrosion resistance, such as stainless steels, nickel alloys and cobalt alloys:

$$\text{PRE} = \% \text{Cr} + 3.3 (\% \text{Mo} + 0.5\% \text{W}) + 16 \% \text{N} \quad (1)$$

The higher the PRE-number the higher the resistance of the chrome containing alloy to localized corrosion promoted by chloride ions. Obviously, Equation 1 cannot be used for brass, Ni-Cu alloys (Monel) or titanium alloys. NACE MR0175/ISO15156-3 does not address the selection of materials external to the Oil & Gas production environment.

In general, the industry separates the application of CRA depending if the CRA has a higher or lower than 40 PRE-number. NACE publication 1F192 discusses the CRA properties based on PRE < 40 and PRE > 40.⁴⁷ Norsok² Materials Selection standard M001 requires that all CRA used in raw seawater need to have a PRE > 40, and they do not need cathodic protection. It is also mentioned that stainless steels with PRE > 40 do not have to be coated under pipe clamps.⁵⁷

The objective of the current manuscript is to explore the effect of the gases CO₂ and H₂S on the localized corrosion of CRA promoted by chloride ions. The relationship between the localized corrosion resistance of CRA and chloride concentration and temperature is rather well known. However, in oil and gas wells containing water and dissolved chloride ions (e.g. of Na, K, Mg, Ca salts), also contain other species such as hydrogen sulfide and carbon dioxide. It is unclear how the presence of either H₂S or CO₂ affect the localized corrosion resistance of CRA in presence of chloride. Do these gases act as inhibitors of localized corrosion? Or do the gases increase the susceptibility of CRA to localized corrosion? Depending on the amount (partial pressure or fugacity) of each gas the system can be classified as sweet (dominated by CO₂) or sour (dominated by H₂S).

CRA for Aggressive Upstream Environments

¹ NACE MR0175 / ISO 15156 (NACE, Houston, TX 2015)

² Norsok Standard M001 “Materials Selection,” Edition 5, September 2014, (Lysaker, Norway)

For aggressive upstream oil and gas applications generally a desirable alloy would be a strong material (i.e. yield stress higher than 700 MPa) with good localized corrosion resistance. Figure 2 shows the localized corrosion resistance as the critical crevice temperature in ferric chloride as a function of the yield stress in MPa. Some mechanically strong alloys from Table 1 have poor corrosion resistance (e.g. 17-4PH) and some alloys with good corrosion resistance have poor mechanical properties (e.g. Ti Gr2).

The most common materials in upstream oil and gas are carbon steels and low alloy steels (LAS), which may represent a 90% of all the volume of metal used. The CRA represent only a small fraction of the alloys. The most popular alloys are martensitic 13Cr, duplex, austenitic stainless and nickel based alloy 718 (N07718). A very small volume of the other CRA are used. Due to their limited localized corrosion resistance, martensitic stainless steels (Table 1) are mainly used in applications with high CO₂ content (which would be corrosive to carbon steel) and with limited amount of hydrogen sulfide. Austenitic stainless steels such as type 304SS are common but in some applications, because of its higher localized corrosion resistance, the use of type 316SS (S31600) is replacing 304SS (S30400).⁵⁸ When resistance to seawater or higher strength is needed duplex SS are popular. Because of its high strength and commercial availability, the use of alloy 718 is rather popular in oil and gas applications, even though its localized corrosion resistance is limited (Table 1 and Figure 2). For example, alloy 718 cannot be used in seawater applications.

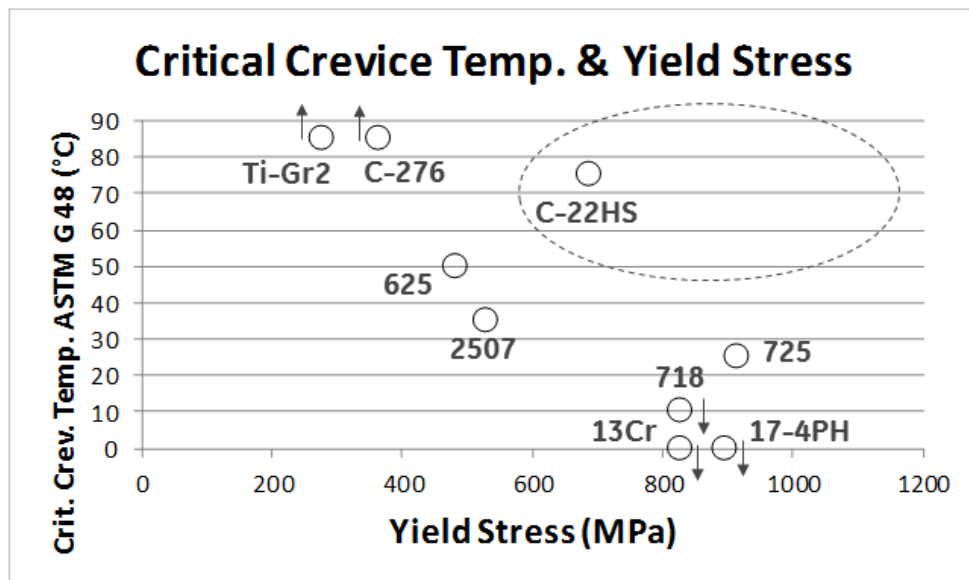


Figure 2: Localized Corrosion Resistance vs. Yield Stress for CRA. The higher the critical crevice temperature (CCT) in the ASTM G 48³ (Ferric chloride methods C&D) environment, the higher the resistance of the CRA to localized corrosion. The ferric chloride solution decomposes at 85°C, that is, values of CCT higher of 85°C cannot be determined. Desirable alloys would be in the dashed oval.

³ ASTM American Society for Testing and Materials, West Conshohocken, PA, USA

**Table 1
Corrosion Resistant Alloys (CRA) Used in Upstream Oil & Gas**

UNS	Type of Material	Approximate Composition, weight %	Typical PRE-Number
S41000	Martensitic	Fe + 12Cr + MN, C	12
S41500 (F6NM)	Martensitic	Fe + 13Cr + 4Ni + 0.7Mo + Mn, Si, C	15
S17400	Precipitation Hardened Martensitic	Fe + 16Cr + 4Ni + 4Cu + 0.3Nb + Mn, Si, C	16
S30400	Austenitic	Fe + 19Cr + 9Ni + Mn, Si, C	19
S31600	Austenitic	Fe + 17Cr + 12Ni + 2.5Mo + Mn, Si, C	25
S44626	Ferritic		25
N07718	Nickel Base Precipitation Hardened	Fe + 52Ni + 19Cr + 3Mo + 5Nb + 1Ti + 0.5Al + Co, Mn, Si, C	29
N08825	Nickel-Iron-Chromium	Fe + 21Cr + 42Ni + 3Mo + 2Cu + 1Ti	31
N08904	Super austenitic SS	Fe + 21Cr + 25Ni + 4.5Mo + 1.5Cu + Mn, Si, C	36
S32750	Duplex SS	Fe + 25Cr + 7Ni + 3.5Mo + 0.3N + Mn, Si, C	41
N08367	Super austenitic SS	Fe + 21Cr + 24Ni + 6.5Mo + 0.2N + Mn, Si, Cu, C	46
R31233	Cobalt base	Co + 26Cr + 9Ni + 5Mo + 3Fe + 2W + 0.08N + Mn, Si, C	47
N06625	Nickel base precipitation hardened	Ni + 21Cr + 9Mo + 5Fe + 3.5Nb + 0.4Al + 0.4Ti + Mn, Si, C	51
N06022	Nickel based, hardened by cold work	Ni + 22Cr + 13Mo + 3W + 3Fe	70
N10276	Nickel base hardened by cold work	Ni + 16Cr + 16Mo + 4W	75
N07022	Nickel base precipitation hardened	Ni + 21Cr + 17Mo + Fe	77
N04400	Nickel-Copper	Cu + 67Ni + Fe, Mn, Si, C	NA
R50400	Titanium	Ti + 0.3Fe + 0.03N	NA

Effect of Hydrogen Sulfide on the Pitting behavior of CRA

Nickel and iron based CRA are susceptible to localized corrosion such as pitting and crevice corrosion because they develop a passivating oxide film on the surface. CRA do not suffer the general corrosion by CO₂ which is the most common degradation mode (sweet corrosion) of carbon steels and LAS. In Oil & Gas environments, and in other environments, the susceptibility of CRA to localized corrosion will be controlled by several factors, which can be grouped into

(a) External or environmental and (b) Internals or metallurgical. The most important environmental factors are: (1) Chloride concentration, (2) Temperature, (3) pH, (4) Redox potential at the in-situ application, (5) Presence of other species such as scaling ions, organic acids, and CO₂ and H₂S gases. The most important internal or metallurgical factor is the alloy composition, which for many alloys is represented by the PRE-number. The PRE-number was initially developed for stainless steels and later its use has been extended to nickel alloys (Table 1). The PRE-number provides information only about the chemical composition of four alloying elements, but it does not specify in what form these alloying elements should be present in the alloy. For example, if an alloy has a high chromium content (e.g. 20%) but a fourth of this chromium (e.g. 5%) is precipitated as carbides or nitrides, only $\frac{3}{4}$ of the chromium (e.g. 15%) may be available to the alloy to provide passivation or protection against localized attack by chlorides.

Olaisson et al. tested the resistance to cracking of duplex stainless steel S33207 (PRE = 50) in a chloride plus hydrogen sulfide environments at 90°C. For four-point bend specimens, they reported that in a solution of 25% NaCl, pH 3 and with a partial pressure of hydrogen sulfide from 3 to 8 psi, the duplex stainless steel specimens were free from pitting corrosion (the balance in the gas pressure was CO₂). In tensile tests in pH 4 environments, when the solution had 25% NaCl and 5 psi partial pressure of H₂S (also balanced with CO₂) the specimens were free from pitting corrosion. However, in a pH 4 solution of 15% NaCl with 7.5 psi of H₂S one of the two specimens suffered slight pitting corrosion.⁵⁹ It is difficult to determine what caused the pitting corrosion, if the increase in H₂S or the decrease in the concentration of NaCl.

Ding et al. studied the corrosion behavior of duplex stainless steel S31803 in chloride environments containing both H₂S and CO₂. They reported that the presence of sulfur species such as H₂S, HS⁻ and S²⁻ in chloride solutions transform the protective oxide films on stainless steel into less protective sulfide films (Fe(Cr)S_x), and therefore promoting pitting corrosion by chloride ions. They reported that as the concentration (pressure) of H₂S - CO₂ increased in a 150,000-ppm chloride solution at 60°C, the susceptibility to localized and general corrosion increased. The localized corrosion always happened in the ferrite or alpha phase. Ding et al. did not separate the effects of H₂S from CO₂.⁶⁰

The localized corrosion risk of duplex stainless steels in sulfide solutions increases when the H₂S and chloride content increase and pH decrease.^{61,62} Azuma et al. performed electrochemical tests of type 316 SS and 22Cr duplex SS in 3.5% NaCl solution deaerated with nitrogen and balanced with 0.01 to 0.1 atm H₂S at ambient temperature and at 45°C, 60°C, and 80°C. The 22Cr duplex SS suffered localized corrosion (crevice and pitting) only in the presence of H₂S while type 316SS suffered localized corrosion in all the tested conditions. The authors also reported that crevice corrosion occurred inside the crevice in the solution without and low H₂S but that the attack shifted to the mouth of the crevice in the most concentrated H₂S environment.⁵⁶

An electrochemical study was performed using type 316L SS in 3.5% NaCl solutions of pH 2.7 (adjusted with 0.5% acetic acid) using three gases: (1) 100% CO₂, (2) 1% H₂S + CO₂ and 1.77% H₂S + CO₂. They reported that H₂S seemed to act as an electron injector into the passive film, therefore hampering the surface film growth by lowering the electric field across the film. The authors argued that by impeding film growth, the presence of H₂S will accelerate the film breakdown of the 316L material.⁶³ Rhodes et al. states that the presence of H₂S in NaCl solutions always increases the pitting and crevice susceptibility of all iron and nickel based CRA.⁶⁴ The detrimental effect of H₂S is both in the increased anodic reaction and in the increased pit acidification due to the precipitation of a stable NiS-rich precipitate.⁶⁵ On the other hand, Newman asserts that there is no concrete evidence that H₂S (and other sulfur species) actually break-down the passive film, for example on type 316SS.⁶⁶

Tsujikawa et al. also reported a decrease of the pitting potential of CRA in sodium chloride solutions as the concentration of hydrogen sulfide increased.⁶¹ They performed pitting corrosion studies in several CRA in 20% NaCl pH 4 solution at 80°C with increasing concentration of H₂S from 0 to 1 atm. In general, Tsujikawa et al. found that levels of H₂S up to 0.01 atm did not produce a decrease in the pitting potential of austenitic alloy 825 (N08825) and duplex SS 2205 (S32205) compared to a saline solution free of H₂S; however, when the H₂S pressure was increased to 0.1 and 1 atm the pitting corrosion could decrease approximately 300 mV.⁶⁷ Uesugi et al. used potentiokinetic and potentiostatic techniques to measure the crevice and pitting potential of ferritic type 444 steel, and austenitic nickel based alloy 625 in 3% NaCl solutions at 80°C under different partial pressures of H₂S.⁶² They reported a decrease in the resistance to localized corrosion of the type 444 steel with increasing H₂S concentrations. They did not find an effect of the H₂S concentration on the localized corrosion of alloy 625 (N06625).⁶⁸

Honda et al. studied the general and localized corrosion behavior of 13Cr and 15Cr steel in 20,000 ppm sodium chloride solutions at 40°C under 2 MPa partial pressure of CO₂ and under varying partial pressures of H₂S up to 0.002 MPa. They reported that the pitting corrosion resistance of 13Cr CRA increased when the partial pressure of H₂S increased from zero to 0.002 MPa. The number and size of the corrosion pits decreased as the partial pressure of H₂S increased. They attributed this increased resistance to pitting on the formation of a FeS film on the surface of the alloy.⁶⁹

The available literature seems to show a detrimental effect of H₂S on the localized corrosion resistance of CRA in chloride environments but results are far from complete. The effect seems to be highly dependent on the resistance to the alloy to localized corrosion (e, g, PRE-value), the concentration of hydrogen sulfide, pH, etc. More research is needed in this area to understand the independent effect of H₂S and CO₂ on the localized corrosion of CRA and the synergistic effect of these two acid gases.

SUMMARY AND CONCLUSIONS

The aim of the paper is to give an update of the knowledge about localized corrosion in sweet and sour environments for carbon steels and CRA. They are the main materials used in oil and gas industry and two completely different scenarios regarding localized corrosion issues.

Plenty of studies have been developed in sweet localized corrosion of LAS and CS during the 1990's. Sour environment corrosion received attention during the last 15 years. Important progress was obtained in the understanding of the protective films. However, the initiation and propagation mechanisms are far from being completely clarified. Pitting is the consequence of a complex combination of factors; the synergistic effect of all these factors is not fully understood and no rules for pitting prediction in CS and LAS are available.

Little published information exists regarding the effect of H₂S and / or CO₂ on the localized corrosion of CRA promoted by chlorides. When studies exist, they generally do not separate the effects of H₂S and CO₂.

In general, it is argued that the presence of sulfur species (such as H₂S) would reduce the resistance of CRA to localized corrosion in the presence of chloride ions. The higher the amount of sulfur species the larger the detrimental effect.

Limited, incomplete and contradictory results exist on the pitting of CRA affected by H₂S - CO₂ in chloride containing environments. The effect seems to be function of the PRE-of the alloy, the pH of the solution, the temperature, and the concentration of the acid gases.

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