# Environmentally Assisted Cracking of Drill Pipes in Deep Drilling Oil and Natural Gas Wells

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Corrosion fatigue (CF), hydrogen induced cracking (HIC) and sulfide stress cracking (SSC), or environmentally assisted cracking (EAC) have been identified as the most challenging causes of catastrophic brittle fracture of drill pipes during drilling operations of deep oil and natural gas wells. Although corrosion rates can be low and tensile stresses during service can be below the material yield stress, a simultaneous action between the stress and corrosive environment can cause a sudden brittle failure of a drill component. Overall, EAC failure consists of two stages: incubation and propagation. Defects, such as pits, second-phase inclusions, etc., serve as preferential sites for the EAC failure during the incubation stage. Deep oil and gas well environments are rich in chlorides and dissolved hydrogen sulfide, which are extremely detrimental to steels used in drilling operations. This article discusses catastrophic brittle fracture mechanisms due to EAC of drill pipe materials, and the corrosion challenges that need to be overcome for drilling ultra-deep oil and natural gas wells.

Keywords	deep drilling, environmentally assisted cracking, high				
	strength low alloy steels, sour gas wells				

### 1. Introduction

The United States' predicted 60% growth in energy demand by 2030 makes oil and natural gas primary target fuels for energy generation (Ref 1). The fact that the peak of oil production from relatively shallow wells (i.e., less than 4572 m (15,000 ft)) is about to be reached is pushing the oil and natural gas industry into drilling deeper wells. The literature data indicate that there are an estimated  $3.2 \times 10^{12}$  to  $3.7 \times 10^{12}$  m<sup>3</sup> (114-132 trillion cubic feet (TCF)) of technically recoverable natural gas resources onshore and another  $1.6 \times 10^{12} \text{ m}^3$ (55 TCF) of recoverable natural gas offshore trapped in reservoirs below 4572 m (15,000 feet) (Ref 2). In addition, deep wells are often very large producers of oil and natural gas relative to their shallow counterparts. However, producing oil and natural gas from these deep wells often means drilling in high-pressure and high-temperature (HPHT) conditions while using dense corrosive muds for which the oil and gas industry does not have full capabilities (Fig. 1) (Ref 3). Till date, the oil and natural gas industry has successfully drilled and completed HPHT wells in Mobile Bay, Thomasville, East Texas, and the New Gulf of Mexico Fields (Ref 4). However, it is expected that still deeper wells will be necessary to tap the available reserves with pressures and/or temperatures higher than those in the Mobile Bay well (Fig. 2) (Ref 5).

Drilling costs for wells deeper than 7620 m (25,000 ft), also called ultra-deep wells, are of a great concern to the oil and gas industry. The oil and natural gas industry bases the ultra-deep drilling (UDD) costs on drilling rates of penetration (ROP). Examples of cost estimates for completed conventional, deep and ultra-deep wells are shown in Fig. 3 (Ref 3). As shown in Fig. 3, the drilling costs increase exponentially with increasing well depths. It costs approximately \$850,000 to drill and complete conventional wells, approximately 1524 m (5000 ft) deep, compared to \$M50 to drill and complete UDD wells. Some reports applicable to deep drilling in the U.S. Gulf Coast indicate that approximately 50% of rig time is spent drilling the last 10% of the hole (Ref 6). Therefore, improving the rate of penetration in the deepest segments of deep well drilling through technological advancements is necessary. These cost estimates do not include unscheduled drilling downtime caused by catastrophic failures of drilling string components, casing, and completion equipment.

It is reported that a drill string failure happens, on average, one out of every seven drilling operations and costs more than \$100,000 per failure event (Ref 7). A downhole failure of the drill string, resulting in complete drill pipe separation, also called twistoff, can be very expensive, especially if it is not possible to recover the remaining part of the drill string from the hole. In such instances, the operators may need to drill a new hole parallel to the section occupied by the broken drill string. The time for completing this unplanned operation, and replacing the broken equipment, may cost upward of one million dollars. Therefore, detecting the presence of holes formed in the drill strings before catastrophic failure will be advantageous for oil and gas drillers, reducing the cost of overall costs associated with drilling the well.

The perforation in the drill pipe, also, called washout, can be very difficult to detect, since it may form at high depths during the later stages of drilling operations and slight changes in pressure and flow rate data can be easily overlooked by the operator. A lot of effort is, therefore, placed on drill string

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Fig. 1 Pressure/temperature regimes for deep and ultra deep oil and gas wells (adopted from Ref 3)



Fig. 2 Examples of off-shore HPHT wells in Gulf of Mexico (adopted from Ref 5)



Fig. 3 Examples of completed well costs (adopted from Ref 3)

design, well geometry stress distribution, etc. Consequently, torque, tension, compression, and bending stresses of a drill pipe (Fig. 4) (Ref 4) can be correctly predicted for a known well geometry. However, any unexpected changes in well geometry during drilling leading to changes in stress distribution, along the drill string and the presence of corrosive species due to the ultra deep well environment, can induce catastrophic failure by fracture. Thus, the potential for catastrophic failures in the HPHT and corrosive environment, containing dissolved hydrogen sulfide (sour environments) and chlorides are considered very seriously by the oil and gas industry. Figure 5 shows an example of environmental condition changes as a



**Fig. 4** Major stress conditions present on a drill pipe (adopted from Ref 4)



Fig. 5 Examples of  $CO_2$  and  $H_2S$  concentrations in oil and natural gas wells for different well depths (adopted from Ref 8)

function of well depth (Ref 8). It can be seen that with the increasing well depth up to 7620 m (25,000 ft), the concentrations of corrosive compounds, e.g., carbon dioxide (CO<sub>2</sub>) and hydrogen sulfide (H<sub>2</sub>S), also increase. At depths approaching 10000 m (>32,000 ft), the H<sub>2</sub>S concentration reaches  $3.2 \times 10^{-7}$ %. No information is given for CO<sub>2</sub> concentration at these extreme depths.

Lack of synergism among the service environment, operational stresses, and materials microstructure can result in catastrophic brittle failures characteristic for environmentally assisted cracking (EAC). Corrosion-resistant alloys of high strength can exhibit increased susceptibility to EAC. Taking into account the high strength required of alloys used in UDD, the drill pipes are more susceptible to EAC, and this poses a significant challenge in improving upon, or developing, new alloys that are economically viable for UDD. In order to do this, it is necessary to understand potential catastrophic failure mechanisms caused by EAC in drill pipes. A lesson-learned approach should serve as a foundation for developing these new alloys that meet stringent requirements for the UDD operations in HPHT corrosive environments.

#### 2. Stress Distributions in Drilling HPHT Wells

Chandler et al. (Ref 9) defined UDD as having a true vertical depth (TVD) greater than 7620 m (25,000 ft) with no more than a total horizontal departure (THD) from the vertical of less than 0.25. This type of drilling imposes a different stress state to the drill string compared with extended reach drilling (ERD), which uses large horizontal departures at shallower depths as shown schematically in Fig. 6. While ERD is considered to be primarily torque dependent, secondary concerns related to tensile stresses are also important. UDD, on the other hand, is primarily tension dependent with secondary concerns related to the torque imposed on the drill string (Ref 9). In a corrosive environment, where fatigue may be accelerated by corrosion, corrosion fatigue (CF) may present a unique challenge because of the higher mean stress during the fatigue cycle. Complicating the situation further is the use of the very high strength alloys for UDD conditions. The susceptibility to sulfide stress cracking (SSC) and/or hydrogen-induced cracking (HIC), while under high tension, is a real concern even when there is little or no fatigue cycling (Ref 10-12).

Material requirements for drill pipe are very stringent in most instances, but especially for UDD operations. As noted, drilling to greater depths generally requires increasing the strength-to-weight ratio of the drill pipe material. For steel drill pipe, this means increasing the yield strength. However,



**Fig. 6** Difference between vertical drilling and extended-reach drilling. Ultra-deep drilling region above 7620 m (25,000 ft) is also shown (adopted from Ref 9)

increasing the yield strength decreases toughness, and for drilling operations, in general, high fracture toughness is also important. Therefore, any steel used in UDD operations must be strong, tough, corrosion resistant, readily available, easily joined, and inexpensive (Ref 9, 13). Finally, drilling to the deeper depths in UDD wells exposes the drill string to elevated temperatures (typically greater than 200 °C, or a  $2 \times$  increase in temperature) and high pressures (typically >100 MPa, or about 3-4× increase in pressure) greater than those found in conventional drilling operations (Fig. 2) (Ref 2, 8).

#### 3. Materials Requirements for Drill Pipes

Steels traditionally used for drill pipes are C-Mn or Cr-Mo type. Drill pipes, in accordance with the American Petroleum Institute (API) 5D specification, have to be seamless and heat treated either by quenching and tempering, or normalizing and tempering, to the required minimum strength. Also, the maximum amount of P or S allowed in the alloy is 0.03 wt.% for each element. Table 1 shows the mechanical properties and heat treatments for different steel grades to meet the required API 5D specification (Ref 14).

Chemical composition ranges for grade E are similar to plain carbon steel (AISI 1041 or 1045) modified with approximately 1.5 Mn and 0.25 Mo. As shown in Table 1, they are either normalized or normalized and tempered: Grades X, G, and S are 4100 series steels in modified (H) form; and Grades X and G have similar chemical composition ranges: 0.2-0.3% C, 1.2-1.5% Mn 0.4-0.6% Cr, and 0.2-0.5 Mo. However, Grade X is usually normalized and tempered, while Grade G is quenched and tempered. Grade S with the highest strength (Table 1) among the four API drill pipes is usually quenched and tempered. Its chemical composition range is 0.27-0.35% C, 1.5-1.6% Mn, 0.1-0.5% Cr, 0.3-0.4% Mo, and 0.012-0.016% V. Also, hardness increases with increasing yield strength of the drill pipes ranging from 20 to 28  $R_{\rm C}$  for Grade E, 27 to 30  $R_{\rm C}$ for Grade X, 30 to 34  $R_{\rm C}$  for Grade G, and 34 to 37  $R_{\rm C}$  for Grade S. The nominal chemical compositions of API steel drill pipes are summarized in Table 2 (Ref 14).

At present, API's Grade S-135 is the industry standard for high strength, low alloy (HSLA) steel. However, drilling to depths greater than 4572 m (15,000 ft) requires increasing the strength-to-weight ratio of the drill pipes materials. The higher strength-to-weight ratio steels under development include Z-140, V-150, and UD-165 drill pipes (Ref 9, 13, 15). Grade Z-140 was specifically developed for use in extreme drilling conditions present in HPHT wells. Grade V-150 was developed for applications that require ultra-high strength steel.

Table 1Mechanical properties and heat treatments for each grade of seamless steel drill pipes as required by API 5Dspecification (adopted from Ref 14)

Grade	Yield strength (MPa/ksi)		Minimum tonsilo	Minimum Charpy impact energy at 21 °C (J/ft-lbf)		
	Maximum	Minimum	strength (MPa/ksi)	1 Sample	3 Sample average	Heat treatment
E-75	725/105	517/75	689/100			Normalized or normalized & tempered
X-95	862/125	655/95	724/105	47/35	54/40	Quenched & tempered or normalized & tempered
G-105	931/135	724/105	793/115	47/35	54/40)	Quenched & tempered or normalized & tempered
S-135	1138/165	931/135	1000/145	47/35	54/40)	Quenched & tempered or normalized & tempered

Grade UD-165 provides a 22% improvement in strength-toweight ratio in comparison to S-135. It is worth noting that Z-140, V-150, and UD-165 are currently not covered by API standards.

For UDD applications, carbon fiber composites, aluminum, and titanium were considered as alternatives to HSLA steels. Each of these materials has some advantages and disadvantages over steel drill pipes. For example, the carbon fiber composite drill pipes are non-magnetic and have lower weight, higher strength-to-weight ratio, and excellent corrosion and fatigue resistance. However, their main disadvantage is their lower hydraulic performance and efficiency associated with pressure losses through the pipe. To have the necessary structural properties (torsional strength, tensile capacity, and pressure integrity), a composite drill pipe must be significantly thicker than the conventional steel drill pipe for the same drilling operation. Depending on the design parameters, the wall thickness of composite drill pipe may be up to twice the wall thickness of comparable conventional steel drill pipe. This results in a significantly reduced inner diameter of the pipe, resulting in unacceptable pressure losses throughout the pipe making it unsuitable for not only for UDD operations but also for extended-reach drilling (Ref 9).

Aluminum drill pipes have been successfully used by the petroleum industry for a long time. Typically, they are made of 2015-T6 aluminum alloy. Their advantages include lower weight, good fatigue, and corrosion resistance to general corrosion at neutral pH. However, there are many disadvantages that include susceptibility to pitting corrosion, severe dissolution at high and low pH values, susceptibility to CF in drilling fluids containing 18% NaCl, and SCC susceptibility in oxygen-containing brines (Ref 14). Also, aluminum yield strength is low (476 MPa) (69 ksi) compared to steel, for example, resulting in low strength-to-weight ratio compared to HSLA steels. Moreover, as temperature increases, yield strength decreases. Since temperatures above 180 °C are expected in ultra deep wells, this makes aluminum drill pipes unsuitable for these operations.

On the other hand, titanium-based drill pipes, for example, Ti-6Al-4V or Ti-3Al-8V-6Cr-4Mo-4Zr Grade 19 (Beta C) have several advantages over API steel drill pipes. These include lower weight, higher strength-to-weight ratio, good corrosion, and fatigue resistance. However, the main disadvantage in using titanium drill pipe is their cost relative to steel. With respect to UD-165 HSLA steel drill pipe, the typical titanium alloys have approximately 15% lower strength-to-weight ratio (Ref 9), and this makes them less attractive for UDD operations.

Table 2Chemical composition of drill pipes meeting API5D specification (adopted from Ref 14)

Grade	Chemical composition (wt.%)			
E-75	1041 or 1045 + 1.2Mn, 0.2Mo, $P \le 0.03$ ,			
	$S \leq 0.03$			
X-95	0.2-0.3C, 1.2-1.5Mn, 0.4-0.6Cr, 0.2-0.6Mo,			
	$P \leq 0.03$ , $S \leq 0.03$ , Fe-balance			
G-105	0.2-0.3C, 1.2-1.5Mn, 0.4-0.6Cr, 0.2-0.6Mo,			
	$P \le 0.03$ , $S \le 0.03$ , Fe-balance			
S-135	0.27-0.35C, 1.5-1.6Mn, 0.1-0.5Cr, 0.3-0.4Mo,			
	$0.012-0.016$ V, P $\leq 0.03$ , S $\leq 0.03$ .			
	Fe-balance			

The disadvantages associated with alternative materials for UDD operations indicate that the industry still needs to rely on the high-strength steels for drilling ultra-deep wells. In order to improve drill pipe reliability and make the drilling process cost effective, it is of the utmost importance limit, or to prevent completely, any catastrophic failures caused during UDD under HPHT conditions. CF, HIC and/or SSC have been recognized as typical forms of EAC that occur under these conditions and they are discussed in more detail in the next section.

### 4. Corrosion Fatigue

The literature data indicate that  $\sim$ 75% of all the drill string failures are caused by fatigue or fatigue-induced mechanical failure. There are two types of fatigue loading conditions experienced by drill strings during operation (Ref 16):

- 1. Rotating-bending when the drill string passes around bends. (1-3 Hz)
- 2. Vibrational fatigue loading including
  - (a) lateral vibration (rattling in the annular gap, 0.5-10s of Hz);
  - (b) tension-vibration (from drill bit stick and slip 0.05-0.5 Hz);
  - (c) axial vibration (impacting hard formation 1-10 Hz).

In general, if a material is stressed repeatedly above fatigue limit, it fails after a certain number of cycles.

Fatigue failures occurring in non-corrosive environments, such as dry air, inert gases, or vacuum, can be caused by extrusions and corresponding intrusions along the metal grains close to the surface due to slip band formation as a result of mechanical deformation. These slip bands result in notch formation and finally cracking. If the cyclic stress is below the fatigue limit, then, work hardening only occurs and failure does not occur (Ref 12).

In order to determine fatigue limits, tests are conducted by subjecting smooth and notched metal tensile samples to cyclic stresses of various magnitudes and plotted as cyclic stress vs. number of cycles to crack initiation or failure. These curves are known as S-N curves (Ref 10, 17).

Typical S-N curves for smooth and notched steel samples are shown in Fig. 7. As can be seen in the figure, the fatigue



**Fig.** 7 Schematic S-N curves of smooth and notched of steel in air (adopted from Ref 10, 17)



Fig. 8 Twistoff of S-135 caused by pitting and fatigue (adopted from Ref 14)

limit is independent of stress at low stress levels. However, the notch presence affects substantially the fatigue limit of a material. The fatigue limit for the smooth sample is higher than that for the notched sample. The applied stress rises at the notch tip and exceeds the yield strength of the material causing a substantial reduction in fatigue strength. Also, the fatigue resistance is directly related to the radius or the sharpness of the notch. The sharper the notch or the smaller the notch radius is, the lower is the fatigue resistance.

Notch depth also affects fatigue resistance. Deeper notches substantially reduce fatigue resistance in comparison to shallow ones. Mechanical notches on the external drill pipe surfaces, made, for example, by tongs and/or rotary slips, can serve as initiation sites for brittle fatigue crack propagation leading to catastrophic drill pipe failure. If the fatigue crack propagates very rapidly in a transverse direction, then twistoff of a drill pipe may occur (Fig. 8) (Ref 14). However, if the fatigue crack propagates relatively slowly and the drilling medium erodes the affected material, then a hole or a washout forms in the drill pipe (Fig. 9) (Ref 18). Washouts usually occur in higher fracture toughness drill pipes, while twistoffs occur in lower fracture toughness drill pipes. Drill pipe twistoff requires laborintensive and time-consuming fishing operations to trip the string in comparison to washouts. Thus, the API and ISO standards recommend minimum fracture toughness determined by the Charpy impact test for higher strength drill pipe grades to avoid twistoff occurrence (Ref 14).

The effect of corrosive environment on fatigue performance of steels can be significant. Figure 10 shows S-N curves generated for 0.18% C steel samples in the presence of aerated 3% NaCl (corrosive environment) and in deaerated water (inert environment) (Ref 19, 20). The results indicate that the presence of the NaCl solutions reduces significantly the fatigue performance of the material. Also, the results indicate that, in the NaCl solution, the S-N curve continues to decrease as the number of load cycles increases, indicating a lack of a definite fatigue limit. This phenomenon is widely observed for steels in



Fig. 9 Washout caused by pitting and corrosion fatigue in a drill pipe (adopted from Ref 18)



Fig. 10 S-N curves of 0.18% carbon steel in deaerated water and aerated 3% NaCl (adopted from Ref 19, 20)

corrosive environments indicating that brittle fracture can occur at very low stress levels, apparently because of a corrosive attack upon the extrusions and intrusions at slip bands created in the surface, preventing work hardening and strengthening of metal (Ref 12). This explains why CF damage is a synergistic action of corrosion and fatigue, and is greater than that caused by the sum of both acting separately (Ref 11). It also explains why corrosion resistance of a metal is more important than high tensile strength in establishing optimum resistance to CF.

Corrosion fatigue is most pronounced at low stress frequencies since a low-frequency cycle results in greater contact time between metal and corrosive solution (Ref 17). This indicates that life of the component is shorter because time available per cycle for corrosion action is also longer. CF occurs, therefore, in all alloys and pure metals and is not specific to certain corrosive environments. Sooner or later, however, in all environments, CF occurs and shows the same variation with different corrosive environments similar to general corrosion.

 Table 3
 Effect of dissolved gases in 5% NaCl on corrosion fatigue of carbon steel (adopted from Ref 21)

Dissolved gas in 5% NaCl	Endurance limit at 10 <sup>7</sup> cycles (MPa/ksi)	Decrease from fatigue limit in deaerated NaCl (%)	
N <sub>2</sub> (deaerated)	207/30	0	
Air	69/10	67	
H <sub>2</sub> S	158/23	24	
$\tilde{H_2S}$ + air	103/15	50	
CO <sub>2</sub>	117/17	43	
$CO_2 + air$	117/17	43	
$\overline{CO_2} + H_2S$	76/11	63	

In particular, CF strength of all steels in NaCl is lower than that in, for example, fresh water. This can be explained by the process of pit initiation due to pitting corrosion and crack propagation. In chloride-containing environments, pits can initiate at inclusions, such as manganese sulfide particles, due to a local chemistry difference between the matrix and the inclusion. Corrosion pits subsequently act as stress risers and initiate cracks. Corrosion dissolution is high at the crack tip, and as a result the crack tip radius changes. Inside the crack, the environment can be acidic due to formation of HCl. Since the radius constantly decreases because of a simultaneous mechanical and corrosion action, CF strength can be quite low. Thus, pitting corrosion in steels and other metals and alloys is of great importance in CF crack initiation. Therefore, alloys with a high resistance to CF must also possess a high inherent resistance to pitting corrosion.

In addition, CF of carbon steel is influenced by the presence of dissolved gases in NaCl. Table 3 shows the highest reduction in CF performance for a drill pipe in aerated 5% NaCl in comparison to dissolved H<sub>2</sub>S. Carbon dioxide dissolved in deaerated or aerated 5% NaCl is equally detrimental to the steel. Dissolved H<sub>2</sub>S in NaCl containing CO<sub>2</sub> further decreases the fatigue limit of the steel (Ref 21). The beneficial effect of solution deaeration on the steel fatigue behavior is shown in Fig. 11. The results show the presence of the fatigue limit in deaerated 5% NaCl and its absence in the aerated solution (Ref 21). This result was also confirmed by Duquette (Ref 19) for 3% NaCl. This indicates that dissolved oxygen plays a major role in the CF mechanism in neutral pH solutions (Ref 20, 21).

The mode of CF failure is usually transgranular without branching and the crack tip is blunt (Ref 10). The final stages of CF for drill pipes are similar to those occurring during fatigue. When a significant portion of the cross-sectional area is compromised the remaining portion is not strong enough to withstand the applied tensile stress and purely mechanical failure takes place (Ref 14).

Corrosion fatigue may be reduced by reducing the stress on the component. This can be accomplished by using a stress reliving heat treatment on the alloy or by shot-peening the surface to induce compressive stresses. Highly polished surfaces with no notches also improve resistance to CF. Low concentration of pitting agents (e.g., Cl<sup>-</sup>) and oxygen, addition of corrosion inhibitors, and pH control (basic) will be very beneficial in reducing CF. For mild steel, deaeration of 3% NaCl restores the normal fatigue limit in air (Fig. 11). In general, coatings (plastic or sacrificial metal) can be helpful as well.



Fig. 11 Effect of dissolved oxygen concentration in 5% NaCl at room temperature on fatigue behavior of AISI-SAE 1035 steel (adopted from Ref 21)

## 5. Hydrogen-Induced Cracking and Sulfide Stress Cracking

In the presence of wet  $H_2S$ , high-strength steels may crack very fast under a different failure mechanism, e.g., HIC/SSC. Hydrogen sulfide forms when calcium sulfate (CaSO<sub>4</sub>) reacts with hydrocarbons, such as methane—CH<sub>4</sub> (Eq 1), ethane— C<sub>2</sub>H<sub>6</sub> (Eq 2), and propane—C<sub>3</sub>H<sub>8</sub> (Eq 3) as shown in the following reactions (Ref 22):

$$CaSO_4 + CH_4 \rightarrow H_2S + CaCO_3 + H_2O$$
(Eq 1)

$$\label{eq:2.1} \begin{split} 1.5 CaSO_4 + C_2 H_6 & \to 1.5 H_2 S + 1.5 CaCO_3 + H_2 O + 0.5 C \\ & (\text{Eq 2}) \end{split}$$

$$2CaSO_4 + C_3H_8 \rightarrow 2H_2S + 2CaCO_3 + H_2O + C \tag{Eq 3}$$

and in the downhole conditions (Eq 4) (Ref 23):

$$4FeS_2 + 4H_2O + 6H^+ \rightarrow 4Fe^{2+} + SO_4^{2-} + 7H_2S_{(aq)}$$
 (Eq 4)

Therefore, sour gas environments are unavoidable during drilling operation in spite of the fact that corrosion inhibitors are continually added to the drilling fluids to "control" the detrimental action of H<sub>2</sub>S. Although H<sub>2</sub>S is not classified as a strong acid, it dissociates sufficiently to yield a minimum pH of  $\sim$ 4 in saturated solutions (Ref 24) according to the following reaction (Eq 5):

$$H_2S = 2H^+ + S^{2-}$$
(Eq 5)

The  $S^{2-}$  anions act as a hydrogen poisons, i.e., they retard recombination of nascent hydrogen atoms on corroding metal surfaces or at the crack tip (Eq 6) obtained from reduction of H<sup>+</sup> (Eq 7) or water (Eq 8):

$$Me \rightarrow Me^{2+} + 2e$$
 (anodic reaction) (Eq 6)

 $H^+ + e \rightarrow H$  (cathodic reaction: acidic solutions) (Eq 7)

 $H_2O + e \rightarrow H + OH^-$ (cathodic reaction: neutral solutions)

(Eq 8)

The  $S^{2-}$  increases the residence time of nascent H, and enhances hydrogen penetration into the metal lattice. Thus, the hydrogen produced plays a crucial role in all modes of hydrogen damage, including HIC/hydrogen embrittlement, hydrogen blistering, and hydrogen attack. The presence of hydrogen in the steel depends on the type of the steel, the microstructure, and inclusion, and the tensile stress distributions. This includes the effect of total pressure of the system and residual stress from working, cold-forming, or welding operations (Ref 25), which can subsequently cause embrittlement, and possibly cracking.

When atomic hydrogen diffuses into the metal but remains in solid solution in the crystal structure, it reduces the metal's ductility and deformability, which is called hydrogen embrittlement. If internal cavities exist, then a catalytic process on the surface may lead to the formation of molecular hydrogen, causing high pressure and blister formation. If a metal is embrittled by hydrogen and is subjected to tensile stresses above a certain critical value, then HIC occurs. The higher the hydrogen content, the lower the critical stress required for the failure. If HIC is caused by the presence of hydrogen sulfide, then the term SSC is used.

The major environmental factors controlling SSC are  $H_2S$  concentration, pH, and temperature. Other environmental factors that may increase susceptibility to SSC include solution composition, flow rates, changes in surface conditions by the presence of corrosion products or non-protective films on the corroding surfaces, and the presence of corrosion inhibitors that could be unstable or act as catalysts for hydrogen diffusion into metal.

In some cases SSC can be reversed if the hydrogen is removed by holding the sample at elevated temperatures for a certain period of time. Figure 12 shows fracture times as a function of applied stresses of uncharged and hydrogen precharged AISI-SAE 4340 steel samples that were held at 150 °C for 0.5 and 12 h, respectively, before testing. For the uncharged sample, fracture time does not increase significantly with decreasing applied stresses. However, for the hydrogen precharged, and subsequently thermally treated samples, the samples time to fracture, also called an incubation time, decreases with increasing applied stresses until it reaches a minimum stress (a plateau) below which failure due to SSC will not occur. The incubation time and minimum stress for HIC increase with increasing baking time. This indicates that a relatively low-temperature baking operation allows some dissolved hydrogen to escape from the alloy. If all hydrogen escaped, the original properties of the alloy would be restored. However, hydrogen damage effects from further hydrogen charging cannot be restored by removal of dissolved hydrogen



Fig. 12 Fracture of AISI-SAE 4340 steel after thermal removal of  $H_2$  at 150 °C for 0.5 and 12 h (adopted from Ref 26)

(Ref 26). The benefit of higher temperature can be used for components that operate continuously above 65 °C. However, that would not apply to components that are cooled below 65 °C during operation (Ref 25).

Since many operations occur at room temperature, the industry has adopted a pH-pH<sub>2</sub>S diagram, known as NACE/ ISO SSC diagram, for "quantifying" the overall aggressiveness of the environment, Fig. 13 (Ref 25, 27). It is worth noting that the diagram was established for the oil country tubular good (OCTGs) for those material grades up to P110. Other higher strength steels and/or welded products can follow a similar trend but the precise location of region boundaries can be different from those noted in Fig. 13, and the boundaries for these newer alloys need to be established.

From Fig. 13, Region 1 (low-sour region) represents a mild environment, e.g., SSC is not expected to occur in steels up to strength P110 even though metallurgical requirements are not met. Region 2 (transition region) is a zone within which some judgment has to be used regarding metallurgical requirements. Region 3 (high-sour region) represents the most aggressive environment, and the one that is the most detrimental to a material's SSC resistance. Steels used in this region must meet all the metallurgical requirements, which include strength limit, uniform hardness distribution across the wall within 10% of the maximum value, and homogeneous microstructure (Ref 25). Although materials are being evaluated according to the accepted industry standards, and recommendations for heattreatment and hardness requirements are specified, and methods of controlling service environments are met, brittle failures due to SSC accelerated crack propagation can still take place. The cracks detected in the material susceptible to HIC/SSC may be transgranular or intergranular with minor branching. Figure 14 shows crack propagation in S-135 after sour service (Ref 28). It is worth pointing out, that SSC and CF do not involve the anodic mechanism of embrittlement required of SCC (Ref 10).

Taking into account that the H<sub>2</sub>S species are always present in drilling fluids, the corrosiveness of drilling fluids must be controlled by using corrosion inhibitors. H<sub>2</sub>S is neutralized by adding alkaline agents, or H<sub>2</sub>S scavengers, to the drilling fluids (muds). Water-based drilling fluids with pH ~ 11 were used in drilling 4777 m (16,000 ft) wells using X-95 (minimum yield strength 655 MPa (95,000 psi) (Ref 29). For drilling 6096 m (20,000 ft) wells, the oil-based drilling fluid containing calcium hydroxide was used with a similar material, e.g., X-95 (Ref 30). Also, the addition of S<sup>2–</sup> scavengers, such as copper carbonate,



**Fig. 13** Regions of environmental severity with respect to sulfide stress cracking of HSLA steels in 5% NaCl, 0.5% CH<sub>3</sub>COOH, 0.4% CH<sub>3</sub>COONa, and  $x_{H_2S}$ ; pH adjustment: HCl or NaOH (adopted from Ref 25, 27)



Fig. 14 Crack propagation in S-135 drill pipe after sour service (adopted from Ref 28)

or zinc carbonate, to drilling fluid prevented brittle failures while drilling 4777 m (20,000 ft) deep wells. However, corrosion inhibitors are not a "catch all" solution for UDD of the well (Ref 31); indeed, cracking that is characteristic of hydrogen embrittlement has been noticed in S-135 drill pipe as shown in Fig. 14.

In general, the embrittling effect of hydrogen is prevalent in iron-based alloys and steels because of the restricted slip capabilities in the predominant body centered cubic (BCC) structure (Ref 10). However, face-centered cubic (FCC) stainless steels and FCC alloys of aluminum, nickel, and copper are more resistant to HIC/SSC because of inherent high ductility and lower diffusivity for hydrogen, but their susceptibility can increase if highly cold worked (Ref 32). Reactive alloys of titanium, zirconium, vanadium, niobium, and tantalum can be embrittled by insoluble or soluble hydrides (Ref 10). All the effects of the conditions described above must be considered when developing a new class of HPHT materials resistant to fatigue, CF, HIC, and SSC for UDD applications.

#### 6. Summary

Corrosion fatigue, hydrogen embrittlement, and stress corrosion cracking have been identified as the major catastrophic failure modes of high-strength steel drill strings. Differentiating these forms of corrosion from one another may be difficult, and therefore, performing laboratory tests in the conditions that simulated service environments are required to have a better understanding of the potential for each type of failure mode. New high-strength materials can then be developed with superior resistance to CF, HIC, and/or SSC.

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