Effects of Inclusions in HSLA Carbon Steel on Pitting Corrosion in CaCl_2

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Susceptibility of high strength low alloy steel to localized corrosion was studied in 6.7 M CaCl_2 for oil and natural gas drilling applications. Results of the immersion and electrochemical experiments showed that the steel is susceptible to pitting corrosion. Optical microscopy investigations of the polished samples revealed that 10% of the surface area was occupied by defects in the form of pits. The energy dispersive X-ray (EDX) and wavelength dispersive X-ray (WDX) chemical analyses revealed higher concentrations of Mn and S compared to the metal matrix in defected areas. These areas served as the sites for development of corrosion pits during both immersion and electrochemical experiments. The fatigue results of the corroded samples indicate that if the pit was the most significant defect, the fatigue crack initiated and propagated at this site.

Introduction

Fatigue and corrosion fatigue (CF) have been identified as major problems in drillstring failures.¹ The occurrence of fatigue failures is partially associated with the design of the tubular and susceptibility of the alloys to pitting corrosion. Usually, the following parameters are being considered for designing a drillstring: ability to withstand tensile stresses, collapse pressure, and torsional stresses. Unfortunately, relatively less attention is given to avoiding fatigue and corrosion fatigue. The most common two sites where fatigue failure initiate are (1) the internal taper of the upset forged region of the pipe body and (2) the threaded connections, both of which are stress concentrating sites that are part of the tubular design.^{2,3} If defects are present on the drill pipe surfaces in the form of undesired inclusions, corrosion pits can form in these defect sites in drilling fluids. Pits can act as stress raisers and serve as initiation sites for fatigue cracks which can then penetrate the pipe wall. This often causes a washout failure where a large hole is formed in the pipe wall. This often causes a washout failure where a large hole is formed in the pipe wall by erosion-corrosion due to the action of the drilling fluid. In the worst cases, the crack propagates until the cross-sectional of the component is reduced to the point where the fracture toughness (K_{IC}) is exceeded and catastrophic fracture takes place, such as twist-off.^{4,5} Twist-off failures are very expensive; therefore, it is of utmost importance to use materials for the drill pipes that are resistant to pitting corrosion.

High strength low alloy (HSLA) carbon steels are widely used for manufacturing drill pipes. The American Petroleum Institute (API) specification for drill pipe steels limits S and P concentration to 0.03 wt.%. The API does not specify the Mn concentration allowed in the HSLA drill pipes steels, and it can be up to 1.9 wt.%. Literature data indicate that for steels containing Mn in sufficiently high concentrations,

manganese-rich sulfides are formed; if the Mn concentration is too low, Fe-rich sulfides are formed.⁶ However, Mn-rich sulfide inclusions were even found in steels containing relatively low quantities of Mn and they served as initiation sites for corrosion pits.

Inclusion geometry affects resistance of steels to pitting corrosion.^{7,8} Spherical sulfide inclusion sites are more resistant to pit formation than elongated ones. In the absence of Mn-rich sulfides, other heterogeneities, such as carbides, grain boundaries, etc., can serve as pit nucleation sites.

Drilling completion fluids can be very corrosive due to their content of chlorides, which accelerate localized corrosion. For example, common drilling completion fluids contain high concentrations of calcium chloride. There are no data available on the corrosion behavior of these materials in CaCl_2 . To fill this gap, resistance of HSHA steels to localized corrosion in concentrated CaCl_2 was studied. Also, the effect of corrosion on fatigue life of the steel was established.

Experimental Procedures

The chemical composition of S-135 grade HSLA steel selected for this research is shown in Table I. The composition was determined in accordance with the CAP-017J and ASTM E 1019⁹ for all elements listed except for nitrogen, sulfur, and carbon. The nitrogen amount was determined by inert gas fusion-thermal conductivity and the amounts of sulfur and carbon by combustion-infrared absorbance.

TABLE I. Chemical Composition [wt%] of S-135

Fe	Cr	Mn	Mo	Al	Ni	Cu	Nb	S	P	B	C	N
Bal	1.39	0.78	0.68	0.03	0.02	0.02	<0.01	0.002	0.006	<0.005	0.26	0.005

To determine microstructure of the steel, a planar sample 2.5 x 2.5 x 0.5 cm was polished to 0.05 μm finish and etched with 2% HNO_3 dissolved in $\text{C}_2\text{H}_5\text{OH}$. To estimate surface percentage occupied by defects, the sample surface was polished to mirror finish and observed under an optical microscope. Then, the largest defects were further characterized by using optical profilometry as a nondestructive method for determining their geometry. Finally, to determine chemical composition of the selected defects, energy dispersive X-ray (EDX) spectroscopy and wavelength dispersive X-ray (WDX) spectroscopy for sulfur chemical analyses were performed.

For the immersion experiments, a hole of 2.54 mm in diameter was drilled near the edge and the interior of the hole was painted with Microstop. Then, the samples were polished with 1200 grit SiC as the final surface finish, cleaned in ethanol and dried. Then, each sample was weighed and suspended on a Teflon string in one liter polypropylene container filled with the 6.71 M non-deaerated CaCl_2 solution at 20°C. The container was closed with samples fully immersed but not touching the container. Visual observations of all the samples were made every 7 days during the four-week period.

The electrochemical experiments were conducted in a flat cell connected to a one liter reservoir through a peristaltic pump. A solution was circulated between the flat cell and the reservoir at 0.4 l/h. To prevent occurrence of unwanted crevice corrosion in the area not exposed to the electrolyte, it was painted with Microstop. All potentials were measured versus a saturated calomel electrode. Platinum was used as the counter electrode. Samples were flat pieces with a circular area of 0.71 cm^2 exposed to the solution. Before each experiment, the sample surface was prepared in the same manner as for the immersion experiments. Prior to each electrochemical experiment, the air-formed

film was removed by applying cathodic potential 30 mV more negative than the open circuit potential (E_{opc}) for 30 sec followed by measuring an open-circuit potential (E_{opc}) for 55 min. To ensure experimental reproducibility, a minimum of two electrochemical experiments were performed at the same conditions.

In the potentiodynamic experiments, the potential was scanned with a scan rate of 1.67 mV/s in the anodic direction from the potential 50 mV more negative than E_{opc} . As a result, anodic polarization curves (potential versus current density) were obtained for each experiment. The reason for analyzing the polarization curves was to determine the presence of pitting potential values. Also, the curves were used to determine values of applied potential (E_{app}) for potentiostatic experiments (current density versus time) and values of applied current density (I_{app}) for galvanostatic (potential versus time) experiments to accelerate pitting corrosion. The cyclic voltammograms obtained in 6.71 M CaCl_2 were used to determine protection potential (E_{prot}). After selected experiments, pit geometry was determined by generating X-Z and X-Y-Z-dimensional optical profilometry maps. Also, this method was used to determine a number pits in a selected area.

Round tensile samples with a gauge length of 1.02 cm and a diameter of 0.51 cm were used for fatigue experiments. The experiments were conducted on polished and pitted samples in laboratory air (humidity ~30-40%) at 23°C under fully reversed loading ($R=-1$) at frequency of 15 Hz. The maximum cycle number was set for 10^6 . For the polished samples, stress amplitude levels of 550, 575, 600, 625, 675, 725 and 775 MPa were used; for the pitted samples 600, 675, 725 and 775 MPa were selected.

Results and Discussion

Surface Characterization

Figure 1 shows microstructure of etched S-135. As it can be seen, the material is martensitic as required by the API 5D specification. Also, Rockwell C hardness of the investigated steel is 35.1 ± 0.1 , which lays in within the hardness range reported in the literature for the S-135 grade.⁵

Optical microscopy surface observations revealed that approximately 0.1% of the surface is occupied by defects. Figure 2 shows X-Y-Z and Y-Z maps for three major defects located in the center of the sample. As it can be seen they are in a shape of pits. Their depth ranges from ~0.6 μm (pit a) to 0.2 μm (pit b). In order to find out if they are pull-outs or inclusions, their microstructure and chemical composition were studied using SEM equipped with EDX and WDX spectroscopies. Figure 3 shows the microstructure of pit a and it was found that it contains several inhomogeneities. For example, several grain boundaries are still visible inside the defect indicating the presence of inclusion with more than one grain. Also, at least three dark oval- shape spots are distinctly visible in the upper part of the defect in addition to a non-continues line located at the matrix-defect interface. Chemical compositions of the above inhomogeneities' were determined by EDX except for S, which was determined by WDX. The oval-shape spots are rich Mn and S indicating the presence of Mn, S-rich inclusions. Also, a Mn, S-rich spot was detected at the defect-metal matrix interface. Chemical analysis of a spot within the grain shows increased concentration of Mn and S in comparison to the metal matrix. Also, pit b has a similar microstructure to pit a, i.e., grain boundaries and round spots are visible. The EDX and WDX analyses in a few locations showed increased concentrations of Mn and S. There is a crack in the lower part of the pit that can serve as the crevice while in

contact with a service environment. The results confirm that the presence of Mn, S-rich inclusions and crevices reduce resistance of the investigated steel to pitting corrosion.¹⁰

Experimental Results

Figure 4 shows an SEM micrograph of a spherical pit formed during immersion in the 6.71 M CaCl₂ at ~20°C for 4 weeks. It appears that the pit was covered with the corrosion products that detached from the pit and precipitated near the pit mouth. The surface inside the pit has a rough texture indicating faster dissolution of iron in certain locations. The quantitative analysis of a site located in the deepest part of the pit by EDX/WDX revealed ~47 at.% Fe, ~31 at.% O, and ~1 at.% S. Absence of Mn and low concentration of S indicates that of (Mn, S)- rich inclusion could dissolve inside the pit according to equation [1]:

Hydrolysis of Fe²⁺ provides the low pH by (equation [2]):

The Fe²⁺ ions are generated during the dissolution of iron (equation [3]):

It is worth noting that equation [3] represents the only anodic process occurring during pitting corrosion. The cathodic process takes place outside the pit and is represented by equation [4]:

The surface outside the pit contains few small blisters indicative of localized corrosion activity. Chemical composition of a few sites showing polishing scratches was very close to the chemical composition of material before the immersion test. This indicates that that propagation of the corrosion pits provided cathodic protection to surface outside the pit.

The XRD analysis of the corrosion products found near the pit mouth identified β-FeOOH as the main phase. Literature data indicate that the passive layer containing this phase is porous and, therefore, not protective.¹⁰ The following mechanism is proposed for the FeOOH formation. Once FeOH⁺ is present inside the pit, it can be oxidized at the pit mouth to Fe(OH)²⁺, which further hydrolyzes to Fe(OH)₂⁺ according to overall reaction [5]:

Finally, Fe(OH)₂⁺ ions react with OH⁻ and precipitate as hydrated rust (equation [6]):

It appears that the mechanism proposed for pitting corrosion of S-135 in the 6.71 M CaCl_2 solution is in a good agreement with the pitting corrosion mechanism of carbon steel in 0.5 M NaCl .¹¹

To determine the pitting potential (E_{pit}) anodic polarization curves were generated in the potentiodynamic experiments with a scan rate of 0.167 mV/s in non-deaerated CaCl_2 . Figure 5a shows two curves obtained in two separate potentiodynamic experiments. As it can be seen, reproducibility of the curves is very good. Anodic current density increases with increasing potential from E_{opc} ($\sim 0.5 \text{ V}_{\text{SCE}}$) to $\sim -0.35 \text{ V}_{\text{SCE}}$. Then, current density is almost constant from $-0.35 \text{ V}_{\text{SCE}}$ to $-0.2 \text{ V}_{\text{SCE}}$. This indicates that S-135 undergoes active dissolution up to $-0.35 \text{ V}_{\text{SCE}}$ with maximum current density approximately $2 \times 10^{-3} \text{ A/cm}^2$. A cyclic voltamogram generated at a scan rate of 1.67 mV/s (Figure 5b) with the vertex potential of $-0.425 \text{ V}_{\text{SCE}}$ does not show the protection potential in the anodic part of the forward potential scan. This indicates that pit can form at any value of potential or current within the anodic region.

Figure 6 shows the potentiostatic results of S-135 in CaCl_2 . The potential applied was $-0.45 \text{ V}_{\text{SCE}}$ and polarization times were varied from 5 minutes to 1 hour. For the same conditions, the number of pits varied and the current was not same. To improve reproducibility of the measuring parameter, a current density of 1 mA/cm^2 was applied and the potential was monitored. The results of the galvanostatic polarization are showed in Figure 7. An example of the optical image of a tensile bar sample after the galvanostatic polarization for 5 minutes is shown in Figure 8. The area of the sample shown is $\sim 0.02 \text{ mm}^2$. There are four major pits visible. The X-Y optical profilometry map for the upper pit indicates that the pit is $3 \mu\text{m}$ wide at the sample surface and approximately $1.5 \mu\text{m}$ deep. In order to determine if galvanostatically accelerated pits can serve as notches for fatigue crack initiation and, therefore, reduce fatigue life, the fatigue experiments followed the galvanostatic experiments. Also, the fatigue performance of the corroded samples was compared to that of the polished (uncorroded) samples.

Figure 9 shows the fatigue curves results for the corroded and polished samples. As it can be seen, for the same stress amplitude the corroded and polished sample failed after a similar number of cycles. Indeed, student's t-tests were performed to compare the means and no statistically significant difference was found at any stress amplitude.¹² SEM investigations of fracture surfaces indicated that for the polished samples the fatigue crack usually initiated at a tool mark that remained from the sample machining as shown in Figure 10. For the corroded samples, all the samples also failed at the tool marks except for one shown in Figure 11 (Stress Amplitude = 600 MPa, Number of Cycles = 172787). Although the pit is wide, it seems that this pit was the deepest among all the defects present prior to the fatigue test. The EDX chemical analysis shows the traces of Ca and Al, which were only detected inside the pit.

This may indicate that the area containing this inclusion was more active than other areas containing only Mn, S-rich inclusions for the pit formation that served as the nucleation site for fatigue crack initiation during the fatigue test. However, it is worth noting that for Stress Amplitude = 600 MPa, one out of three samples tested did not fail after 10^6 cycles and another sample failed after 7×10^5 cycles. In the latter case, the tool mark served as the initiation for the former.

Conclusions

Optical profilometry, SEM and EDX/ WDX results reveled presence of Mn, S- rich inclusions in S-135 samples.

Immersion and electrochemical results indicate that S-135 is susceptible to pitting corrosion in 6.7 M CaCl_2 .

Fatigue results for corroded and polished S-135 samples indicate that pits have no significant effects on fatigue life.

Pit containing traces of Ca and Al served as initiation site for fatigue crack initiation indicating presence of more detrimental defects that Mn, S-rich defects.

In absence of pits that are deeper than tool marks, tool marks serve as initiation site for fatigue crack development.

Figure 1. Microstructure of etched S-135.

Figure 2. X-Y-Z (a) and X-Y (b) profile maps of surface defects in shape of pits (pit a-deepest; pit b-shallowest) on polished S-135 sample surface.

Figure 3. Backscattered electron images for deepest (a) and shallowest (b) pits shown in Figure 2.

Figure 4. Secondary electron image of pit macrostructure and surrounding matrix on S-135 surface after immersion in 6.71 M CaCl_2 for 4 weeks. Indicated compositions of iron, oxygen, and sulfur in atomic percent.

(b)

Figure 5. Anodic polarization curves at scan rate=0.166 mV/s (a) and cyclic voltammogram at scan rate=16.67 mV/s for S-135 in CaCl_2 . Note reproducibility of polarization curves in (a) and no E_{prot} in anodic region in (b).

Figure 6. Potentiostatic polarization curves for S-135 in CaCl_2 for polarization time up to 1 hour. $E_{\text{app}} = 0.42 \text{ V}_{\text{SCE}}$.

Figure 7. Galvanostatic polarization curves for S-135 in CaCl_2 up to 300 sec. $I_{\text{app}} = 10^{-3} \text{ A/cm}^2$

Figure 8. Three-dimensional (a) and two-dimensional (b) profile maps of S-135 after galvanostatic experiment in CaCl_2 ; $I_{\text{app}} = 10^{-3} \text{ A/cm}^2$, $t = 5 \text{ min}$.

Figure 9. Fatigue curves of corroded and polished S-135 tensile samples. Note that fatigue tests were terminated after 10^6 cycles and arrows indicate that samples did not fail (run-outs).

Figure 10. Secondary electron image showing fatigue failure of S-135 initiated from corrosion pit accelerated galvanostatically in CaCl_2 . Indicated compositions of aluminum and calcium in atomic percent.

Figure 11. Secondary electron image showing fatigue failure of polished S-135 initiated from tool mark seen as a surface scratch on the left side.

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