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HIC and SSC of Carbon Steel in High Partial Pressure CO_2 Environments with Elevated H_2S

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Abstract: The Hydrogen Induced Cracking (HIC) and Sulfide Stress Cracking (SSC) behaviours of sour service and non-sour service carbon steel API 5L X65 were investigated under high pressure carbon dioxide environments, containing elevated amount of hydrogen sulphide (H_2S); the test environments simulated offshore pipelines transporting full-well streams in high carbon dioxide (CO_2) environments with elevated H_2S concentrations. It was systematically studied under standard NACE condition and high pressure carbon dioxide field condition with variation in other key parameters (temperature, pressure and hydrogen sulfide concentration). The HIC and SSC were tested using a High Pressure and High Temperature (HPHT) Autoclave. The surface cracking morphology was analysed using Scanning Electron Microscopy (SEM), Ultrasonic Technique (UT) and Magnetic Particle (MP). The results showed that no cracks were detected in NACE standard and field-condition SSC tests for both sour service and non-sour services carbon steel. In HIC test, crack was detected on non-sour service carbon steel in NACE standard test while no crack was detected on field condition-based tests for both types of carbon steel.

Keywords: HIC, SSC, carbon steel, high CO_2 environment

1 Introductıon

Pipelines made from carbon steel are susceptible to HIC and SSC in wet hydrogen sulfide environment in transporting large amount of hydrocarbon gas with CO_2. Wet hydrogen sulfide cracking is commonly classified into three categories based on initiation, morphology and stress requirement in cracking: HIC, SSC, and Stress Oriented Hydrogen Induced Cracking (SOHIC).

HIC is a form of tiny blistering damage caused by a high concentration of hydrogen in steel. The blistering damage tends to form parallel to the surface and to the direction of hoop stress. Because of this, it usually does not become damaging until it either becomes extensive and affects material properties or gives rise to cracking that propagates into a weld or begins to go stepwise through the wall. On the surface, HIC often appears horseshoe shaped with a size being no bigger than the cuticle of one's small finger. Compared to HIC, SSC occurs at locations where atomic hydrogen can diffuse at sites of high internal stress, such as grain boundaries, inclusions and regions of triaxle stress at notches. When placed in proximity to tensile stress, embrittlement and the beginnings of brittle fracture may occur.
In the oil and gas industry, steels are used for different applications and are consequently exposed to various media. Gaseous or dissolved H_2S is often encountered in production and process fluids. The actual physical/chemical H_2S state will depend on pH, temperature, and partial pressure. Material selection is based on the environmental conditions and must be carried out according to the guidelines given in the NACE MR0175-ISO15156 standard (2015).

Many researchers have reported on corrosion behavior of carbon steel in high partial pressure CO_2 environment either in sweet or sour conditions [1-6], but none has reported on HIC and SSC in the environment containing both high CO_2 and elevated H_2S. For the service to be considered a sour service, the partial pressure of H_2S should reach above 0.05psi. This study investigated the HIC and SSC behaviour of sour service and non-sour service carbon steel API 5L X65 under high pressure CO_2 environments, containing elevated amount of H_2S, to simulate the condition of high CO_2-containing natural gas offshore pipeline. The surface cracking morphology was analysed using Scanning Electron Microscopy (SEM), Ultrasonic Technique (UT) and Magnetic Particle (MP).

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2 Methodology

2.1 Materials

The material used in this work was API 5L X65 carbon steel for sour service and non-sour service. The chemical composition of both types of steels is given in Table 1 below. Based on API Spec 5L, the pipeline steel used for sour service pipe is purity fully killed steel while non-sour service line pipe steel material is grain-killed steel. It shall be noted that the sour service pipe has high purity of steel so as to avoid inclusion sites. The steel can guarantee low S, P and other impurities.

Table 1. Chemical compositions of API 5L X65 used in the present study (balance Fe).

	C	Cr	Mn	P	S	Si	Cu	Ni	Mo	Al	Nb	Ti	V	N	Ca
Sour service X65(I)	0.035	0.24	1.42	0.0055	0.0013	0.16	0.17	0.27	0.09	0.029	0.034	0.011	0.039	0.005	0.0018
Non-sour service X65 (II)	0.05	0.13	1.52	0.007	0.001	0.17	0.012	0.1	0.01	0.026	0.039	0.013	---	0.0027	0.0019

As shown in Figure 1, the specimens for HIC test were machined from both X65 (I) and X65 (II) plates (thickness ≈ 3 cm) with a size of 10 cm × 2 cm × 3 cm as recommended by NACE Standard TM0284-2003[7]:

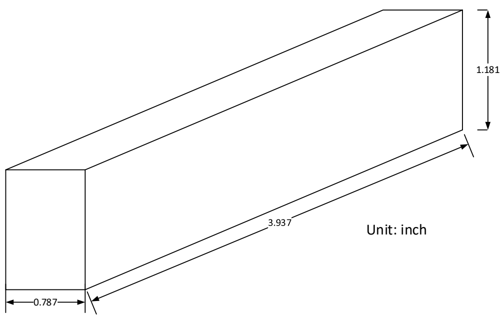

Fig. 1. Samples used for HIC test

Specimens with the same thickness were used to eliminate thickness effect. The specimens were ground up to 320-grit silicon carbide (SiC) paper, rinsed with deionized water, cleaned with isopropyl alcohol in an ultrasonic bath, and dried using a heat gun.

The specimens for C-ring SSC test were machined from both X65 (I) and X65 (II) plates as shown in Figure 2 as per ASTM Standard G38-01[8]:

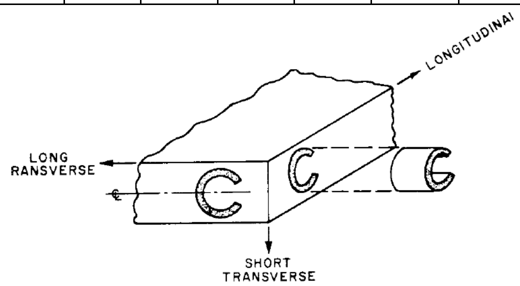

Fig. 2. Sampling procedure for C-ring SSC test specimen.

Figure 3 shows a dimension of C-ring sample used in the present study:

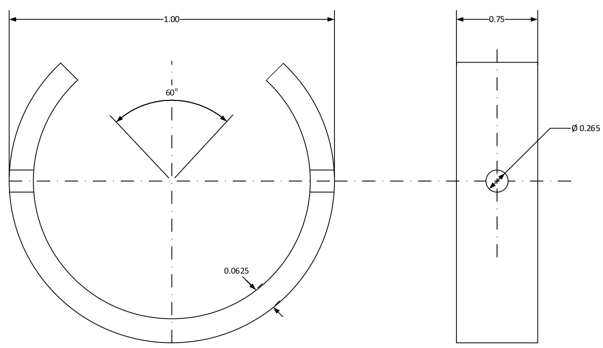

Fig. 3. Dimensional drawing of the C-ring SSC test specimen

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The deflection necessary to obtain desired stress on the C-ring SSC specimen was calculated using the following equation:

$$D = \frac{\pi d(d-t)S}{4tE}$$

where:

D= deflection of C-ring test specimen across bolt holes;
d= C-ring test specimen outer diameter (1");
t= C-ring test specimen thickness (0.0625");
S= desired outer fiber stress (90% and 80% of yield stress);
E= elastic modulus (207 GPa).

C-ring SSC test specimens were stressed by tightening bolting fixtures to the calculated deflections as measured by Vernier caliper. Four C-ring SSC samples with two stress levels, namely 80% yield strength (YS) and 90% YS were placed on the sample holder, specially designed for the test as shown in Figure 4 below:

Fig. 4. C-ring SSC samples with sample holder: 2 samples from X65 (I) and 2 samples from X65 (II).

2.2 Equipment and Test Conditions

The experiments made use of a 5-L high pressure and high temperature (HPHT) Hastelloy autoclave as shown in Figure 5 below:

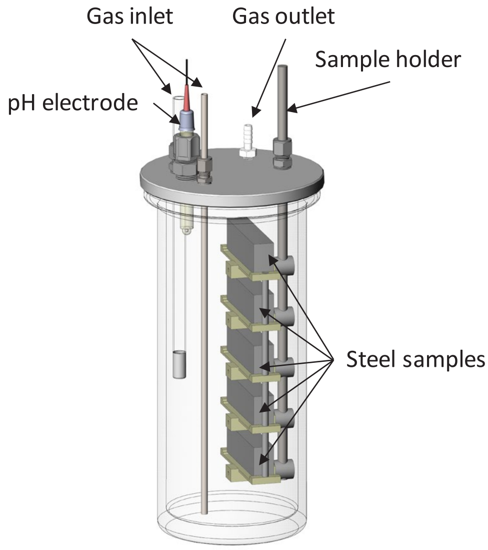

Fig. 5. The 5-L Hastelloy autoclave assembly used in the experimental setup for HIC test.

The experimental conditions for HIC test performed within this study are shown in Table 2 below:

Table 2. The test matrices for HIC experiments

Condition	Material	Solution	pH	Test gas	Pressure (bar)	Temperature (°C)	Duration (day)
NACE	X65 (I) X65 (II)	Solution A (5 wt.% NaCl + 0.5 wt.% CH_3COOH)	2.8	100% H_2S	1	25	4
Field	X65 (I) X65 (II)	1 wt.% NaCl	3.1	2000 ppm H_2S	120 (CO_2)	25	4
Field	X65 (I) X65 (II)	1 wt.% NaCl	3.2	2000 ppm H_2S	120 (CO_2)	80	4

HIC tests were conducted under standard NACE and field conditions. For NACE condition, it followed NACE standard TM0284-2003[7]. Solution A was prepared from deionized water and contained 5 wt.% NaCl and 0.5 wt.% CH_3COOH. The test solution was initially purged with N_2 gas until dissolved oxygen concentration was reduced to lower than 10 ppb. Then, the specimens were immersed in the solution which was saturated under 1 bar H_2S at 25°C. The initial and final pH values were checked, and no pH adjustment was made during the test. The ratio of the volume of test solution (4L) to the total surface area of the test specimens was higher than 3 mL per cm^2. The test duration was 4 days. After the

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exposure period, the extent of HIC was determined by UT and SEM. As for field condition, the test conducted to simulate actual pipeline transportation with 2000ppm H_2S in produced water with 1 wt.% NaCl and pressure at 120bar CO_2. The temperaure of inlet pipeline is 25 ^oC and the outlet of pipeline is 80 ^oC.

Similarly, SSC tests were also conducted under standard NACE and field conditions. SSC test for the NACE condition was based on NACE standard TM0177-2016 Method C- Standard C-ring test [9]. Test solution A was prepared from deionized water and contained 5 wt.% NaCl and 0.5 wt.% CH_3COOH. The test solution was initially purged with N_2 gas until dissolved oxygen concentration was reduced to lower than 10 ppb. Then specimens were immersed in the solution which was saturated under 1 bar H_2S at 25^oC. The initial and final pH values were checked, and no pH adjustment was made during the test. The ratio of the volume of test solution (4L) to the total surface area of the test specimens was higher than 30 mL per cm^2 as recommended in the standard. The test duration was 30 days. Figure 6 shows a schematic of the experimental setup for SSC test. For field condition, the test conducted to simulate actual pipeline transportation with 2000ppm H_2S in produced water with 1 wt.% NaCl and pressure at 120bar CO_2 and temperature outlet of pipeline is 80 ^oC.

At the end of the experiment, the specimens for HIC and SSC were rinsed with deionized water, washed with iso-propanol, and dried using a heat gun. Surface analysis was carried out using SEM, UT and MP.

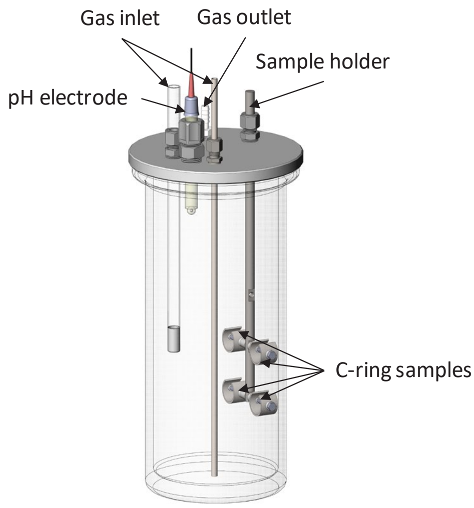

Fig. 6. The 5-L Hastelloy autoclave assembly used in the experiments setup for SSC test.

Table 3 shows the test matrix for SSC tests:

Table 3. The test matrices for SSC experiments

Condition	Material	Solution		Applied stress	Test gas	Pressure (bar)	Temperature (^oC)	Duration (day)
NACE	X65 (I) X65 (II)	Solution A (5 wt.% NaCl + 0.5 wt.% CH_3COOH)		90% YS 80% YS	100% H_2S	1	25	30
Field	X65 (I) X65 (II)	1 wt.% NaCl		90% YS 80% YS	2000 ppm H_2S	120 (CO_2)	80	30

3 Results and Discussion

Table 4 represents the results of HIC test under different conditions:

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Table 4. Summary of the results of HIC test.

Condition	Material	Solution	Test gas	Pressure (bar)	Temperature (°C)	Duration (day)	Crack
NACE	X65 (I)	Solution A	100% H_2S	1	25	4	No
	X65 (II)						**Yes**
Field	X65 (I)	1 wt.% NaCl	2000 ppm H_2S	120 (CO_2)	25	4	No
	X65 (II)						No
Field	X65 (I)	1 wt.% NaCl	2000 ppm H_2S	120 (CO_2)	80	4	No
	X65 (II)						No

Internal HIC crack was only detected from non-sour service X65(II) in standard NACE condition due to the pipeline being non-resistant to HIC attack as compared to sour service X65(I). For field condition simulations, no cracks were observed in all conditions even though the partial pressure of H_2S was more than 0.05psi. It is noted that the CO_2 environment was dominant in field condition even though the partial pressure H_2S was in sour service region based on NACE MR0175-ISO15156 standard (2015). Therefore, no cracks were observed in all the field condition experiments.

Figure 7 shows the results of ultrasonic A-scan inspection of HIC on X65(II) samples exposed to standard NACE condition:

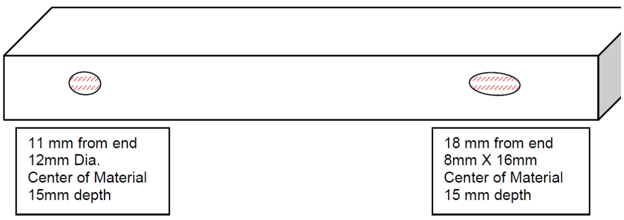

Fig. 7. Results of ultrasonic inspection after HIC test for sample X65(II).

The depth of the indications showed that the cracks were mainly located in the centerline. In order to further investigate the extent of HIC, further analysis was conducted by cutting the crack sample identified by ultrasonic technique. Figure 8 shows SEM pictures of cracks observed on the sample X65(II). It shows multiple cracks as well as some blistering.

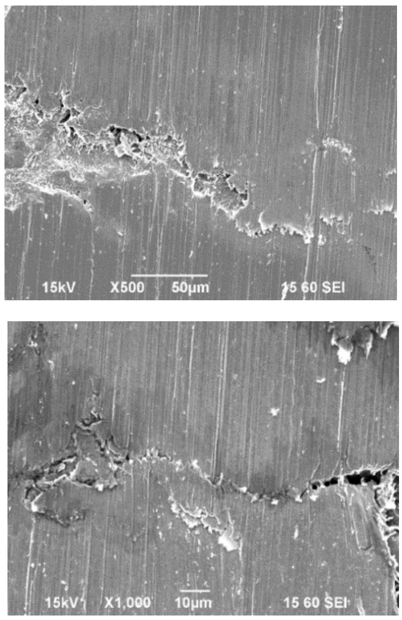

Fig. 8. SEM image of cracks on the sample X65 (II)

Table 5 represents the results of SSC test under different conditions in which no surface crack was observed from all the tested conditions:

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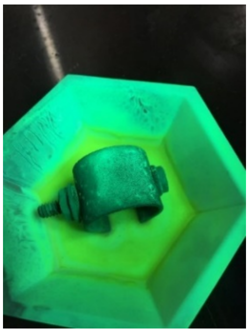
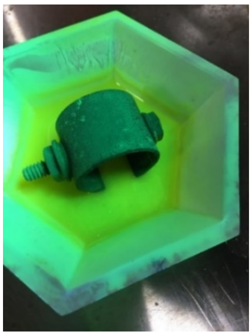
Table 5. Summary of the results of SSC test.

Condition	Material	Solution	Applied stress	Test gas	Pressure (bar)	Temperature (ºC)	Duration (day)	Crack
NACE	X65 (I)	Solution A	90% YS	100% H_2S	1	25	30	No
			80% YS					No
	X65 (II)		90% YS					No
			80% YS					No
Field	X65 (I)	1 wt.% NaCl	90% YS	2000 ppm H_2S	120 (CO_2)	80	30	No
			80% YS					No
	X65 (II)		90% YS					No
			80% YS					No

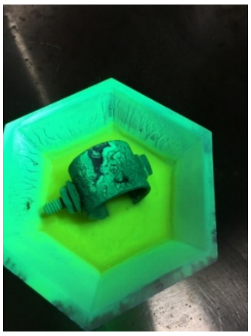
At the end of experiment, the samples were chemically cleaned by Clarke solution in order to remove the corrosion products. After cleaning, the samples were checked by MAGNAFLUX in order to detect macro surface cracks. Figure 9 shows standard condition SSC test pictures of the samples with black light after applying magnetic particles. No surface macro cracks were observed from all samples. The samples were also observed by SEM in order to investigate the presence of micro cracks. No micro cracks were detected from all samples either.



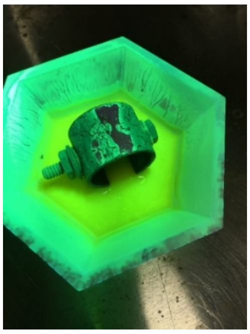
(a)



(b)



(c)



(d)

Fig. 9. Pictures of samples under magnetic particle analysis: (a) X65 (I), 90% YS, (b) X65 (I), 80% YS, (c) X65 (II), 90% YS, (d) X65 (II), 80% YS.

For the C-ring samples exposed to the field condition, the samples were also observed by MAGNAFLUX and SEM. Figure 10 shows SEM pictures of the samples after cleaning. Both pictures show general corrosion, but no micro cracks were detected from all samples.

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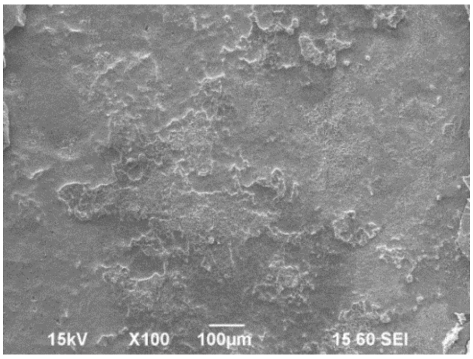
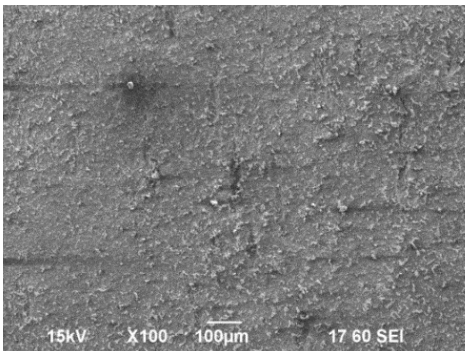


(a)



(b)

Fig. 10. SEM images of cleaned C-ring SSC samples after exposing to 120 bar CO_2, 80°C and 2000 ppm H_2S condition for 30 days: (a) X65(I), 90% YS, (b) X65(II), 90% YS

Conclusions

Thus, the above results suggest the following:

1. Multiple cracks and blistering were observed on X65 (II) carbon steel (non-sour service) from the HIC test following NACE Standard TM0284-2003.
2. No macro/micro cracks were found on X65(I) carbon steel (sour services from the HIC test field condition.
3. No macro/micro cracks were found on both X65 (I) and X65 (II) from C-ring SSC test following NACE Standard TM0177-2016 and field condition.

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