Investigating the influence of flowing fluid on the resistance of materials to sulfide stress cracking

R Rihan¹,², B Al-Wakaa¹ and N Tanoli¹
¹Petroleum Research Center, Kuwait Institute for Scientific Research, Al-Ahmadi, Kuwait
E-mail: rihanr@gmail.com

Abstract. The study aims to investigate the effect of flowing fluid on the susceptibility of metals and alloys to sulfide stress cracking (SSC) using the fracture mechanics circumferential notched tensile (CNT) specimen. The CNT specimen has never been used in the presence of flowing fluid. A novel testing flow loop was invented for performing the experimental work. The new testing rig can be used for determining the stress intensity factor (K_I), threshold stress intensity factor (K_Issc), and crack growth rate in flowing fluid for different materials in different corrosive environments at different temperatures. The testing flow loop has been registered as a patent in recognition of its novelty and practical applications in several industries. The experimental conditions were testing the resistance of heat treated P110 steel to SSC in deaerated stagnant and flowing solution containing 0.01 M Na₂S₂O₃ (as a source for H₂S) and 3.5 w% NaCl at room temperature. The experimental results show the heat treated P110 steel was susceptible to SSC in stagnant solution, while it was not susceptible in flowing fluid.

1. Introduction
Environmental stress corrosion cracking (SCC) is considered to be a very dangerous form of failure, as corrosion cracks may propagate undetected leading to leaks or sudden failure events in the presence of stress and a corrosive environment.

The experience of various industries calls for a new method to investigate the collapsed parts and develop a simple censoring method. The precise censoring of the stress corrosion crack progress and lifetime estimation can be conveyed by the fracture mechanics methods. Though, the conventional fracture mechanics methods are prohibitively expensive and time-consuming, which restricts their use as a commonly used technique for the SCC monitoring. This study aims to use a recently introduced technique to investigate SCC fracture mechanics of circumferential notched tensile (CNT) specimen [1-10], which is a simple and cost-effective technique for evaluating the SCC susceptibility of engineering materials. A usual CNT specimen (figure 1) is one of the smallest achievable specimens that can generate valid plane strain conditions. The cost of each test can be reduced to around 10% by this technique. Rihan et al. [11, 12] has invented two novel CNT test rigs to test the susceptibility of engineering materials to SCC in stagnant (not flowing) fluid. The two CNT rigs were registered as patents [11, 12].

The CNT specimen technique has been successfully utilized for generating threshold stress intensity factor (K_Issc) data for different materials [1-10]. The obtained K_Issc data utilizing the CNT specimens [1-3, 9] were found to be too near to those obtained utilizing other standard fracture mechanics specimens [13-17].
Figure 1. The CNT specimen (all dimensions in mm).

Usually the SCC/SSC tests are performed in solutions at stagnant condition, which is not the case in most of the actual industrial operating conditions where the fluids are moving in industrial equipment and components such as: pipes, tubes, pressure vessels, and heat exchangers. Therefore, it is essential to investigate the susceptibility of alloys to stress cracking in moving fluid in order to simulate the actual operating conditions and get a real indication on the stress cracking susceptibility.

To the best of our knowledge, a few experimental studies [18-22] were performed on the effect of fluid flow velocity on SCC. The results of these studies, generally, indicate that the SCC susceptibility decreases in the presence of flowing fluid and decreases with increasing fluid velocity.

In these studies, the conditions of the flowing solution inside the autoclave were offered by a rotating stirrer, and the accurate orientation of the flow and flow rate over the specimen surfaces (including the crack mouth) was not evaluated. In its place, the flow rate was specified by the stirrer rotation rate. Therefore, it can be concluded that no fracture mechanics study was conducted at a known flow rate or fluid velocity.

The aim of this work is to investigate the effect of flowing fluid on the susceptibility of P110 steel to stress cracking, using the CNT specimen. In order to accelerate the experimental work, the P110 Steel was heat treated to make it more susceptible to SCC. In order to perform the experimental work in flowing fluid, a novel SCC testing rig was designed and constructed for this study.

The test environment contains H₂S since H₂S has been accepted as one of the chief causes of the failure of pipeline materials [23, 24]. The resistance of materials to SSC is frequently the principal factor affecting the selection of materials for H₂S containing environments, since its occurrence can result in a catastrophic and potentially dangerous failure [25, 26].

The CNT specimens were fabricated from P110 steel, which is broadly used as a tubing material for oil and gas wells. Accessible information in the literature is limited concerning the resistance of P110 steel to SSC [27-30].

The experimental conditions comprised testing the susceptibility of heat treated P110 steel to SSC in deaerated fluid consisting of sodium thiosulphate (Na₂S₂O₃), as a source for H₂S, and sodium chloride (NaCl) in flowing fluid at room temperature. Also, experiments at stagnant fluid were performed to determine whether the stress cracking susceptibility is affected by the presence of flowing fluid.

2. Experimental details
A novel SCC/SSC testing rig has been designed and constructed to conduct the experimental work. The testing rig is a flow loop that consists mainly of test sections, autoclave, pump, and flowmeter as shown in figure 2. The testing rig has four test sections connected in series which produce constant flow rate in the test section line. The new SCC testing flow loop has been registered as a patent [31].

The main component of the testing flow loop is the test section. The test section (shown in detail in figure 3) is the most important part of the flow loop. The test section contains the CNT specimen and mimics the existing corrosive environment in industry. Four test sections were built in order to test more specimens at the same time. Each test section has different flow velocities by fabricating the test sections with different flow channel diameters. Four test sections were fabricated as shown in figure 3.
In order to investigate the susceptibility of the test material to SSC in flowing fluid, two tests were performed. One test was performed at the stagnant fluid condition, while the other test was performed at flowing fluid in order to determine the effect of the fluid velocity on the susceptibility of alloys to SSC. Only two to three different values of stress intensity factor ($K_I$) data were obtained for each test, since these types of tests are time-consuming. The duration of the test (time to failure) depends on the value of the applied $K_I$ that may last for a few hours at high $K_I$ values (close to critical stress intensity factor ($K_{IC}$)) or months at low $K_I$ values (close to $K_{ISCC}$). The time to failure ($t_f$) is mainly affected by the applied $K_I$ value, concentration of the corrosive solution, temperature, and material.

The test material was the heat treated P110 steel, which is commonly used as a tubular material by oil and gas industries. The test fluid was a deaerated fluid consisting of 0.01 M Na$_2$S$_2$O$_3$ and 3.5 % NaCl. The pH of the solution was 6.2. Sodium thiosulphate (Na$_2$S$_2$O$_3$) can be used as a substitute for H$_2$S since H$_2$S is a toxic flammable gas and handling it requires special safety measures. This novel approach was first proposed by Tsujikawa et al. [32], where they used Na$_2$S$_2$O$_3$ for a study on the SCC of low alloy steels and found that the results agreed with those for solutions containing H$_2$S. Recent studies [33,34] found that the H$_2$S generation rate was the maximum for the 0.01 M Na$_2$S$_2$O$_3$ concentration. The partial
pressures of H$_2$S in a solution containing 0.01 M thiosulfate is 1.5 kPa [33].

The experiments were performed at room temperature. This temperature was selected since the resistance of steels to SSC in fluids containing H$_2$S is minimum at nearby the room temperature. The SSC resistance increases at temperatures below and above the room temperature [35].

Two experimental series were performed at two velocities; 0 m/s (simulating stagnant fluid condition) and 1.25 m/s (simulating flowing fluid).

The P110 steel was heat-treated to get a higher hardness and yield stress, in order to make it more susceptible to SSC by heating the steel at a temperature of 835°C for ½ h, followed by quenching in water and tempering at 330°C for 2 h [1-3, 14, 17]. The CNT specimens have been fatigue cracked (pre-cracked) by subjecting the CNT specimen to bending and rotation.

3. Results and discussions

In Experimental Series 1, the specimens fractured in very short period of time (9 – 70 h). This remarkably expedited fracture could be due to SSC. The calculated $K_I$ values were plotted against the $t_f$ (figure 4). The method of calculating the $K_I$ values for the CNT specimens is illustrated in previous works [1-10, 36].

![Figure 4. $K_I$ versus $t_f$ of heat treated P110 steel in stagnant and flowing fluid.](image)

The Experimental Series 2 was performed at a flow velocity of 1.25 m/s. None of the specimens failed despite the long testing time (2273 h). The fact that none of the specimens failed in the presence of flowing fluid notwithstanding the very long contact time (2273 h) indicate that the heat-treated P110 steel is not susceptible to SSC in flowing fluid at the applied $K_I$ values. The calculated $K_I$ values were plotted against the duration time (figure 4).

The failure of the test specimens in stagnant fluid can be related to the increase of the concentrations of H$^+$ and/or Cl$^-$ in the internal environment of the crack due to the occluded cell corrosion which decrease the re-passivation rate at the crack tip that lead to the dissolution enhancement at the crack tip [19, 37, 38].

The non-failure of the test specimens in flowing fluid can be related to the flowing fluid that passes the crack mouth that tends to wash out the crack, thus reducing the aggressiveness of the solution of the crack enclave, which in sequence leads to a reduction in crack growth rate [19].
4. Scanning electron microscopy (SEM)
The surfaces of the failed specimens were inspected utilizing SEM. The existence of both intergranular crack propagation and secondary cracking (figure 5) was verified by the SSC. The fracture of heat-treated specimens was the result of the existence of intergranular cracking features (figure 5).

![Figure 5. Intergranular crack propagation and secondary cracking, which confirm the intergranular cracking.](image)

The CNT specimens, which were tested in flowing fluid, were pulled apart and the surfaces of the CNT specimens were inspected by SEM. The SEM images show no signs of intergranular crack propagation, which indicates that the test material is not susceptible to SCC in flowing fluid.

5. Conclusion
- There were failures in the specimens tested in stagnant fluid which indicate that the heat-treated P110 steel is susceptible to SSC.
- The failure of the test specimens in stagnant fluid can be related to the decrease in the repassivation rate at the crack tip due to the increase in the concentrations of H\(^+\) and/or Cl\(^-\) in the internal environment of the crack.
- The experimental results at flowing solution reveal that none of the specimens fractured in the presence of the flowing solution, which can give an indication that the heat-treated P110 steel is not susceptible to SCC in flowing fluid at the applied K\(_{Ic}\) values.
- The non-failure of the test specimens in flowing fluid can be related to the reduction of the aggressiveness of the solution of the crack enclave since the flowing fluid that passes the crack mouth tends to wash out the crack.
- The CNT testing is simple and economical technique for generating K\(_{Ic}\) data.

Acknowledgments
The authors would like to acknowledge the support received from the Kuwait Foundation for the Advancement of Sciences (KFAS), and the support received from the management of the Kuwait Institute for Scientific Research (KISR) by funding this work through Project No. PP053K.

References
[1] Rihan R, Singh Raman R, Ibrahim R and Gerrard D 2006 Determination of the threshold stress intensity factor (K\(_{Ic}\)) of 4340 steel using small circumferential notched tensile (CNT) specimens Proc. Corrosion and Prevention Conf. "Steel and Concrete - Nothing Lasts
“Forever” (Hobart, Australia)

[2] Singh R R, Rihan R and Ibrahim R 2007 Mater. Sci. Eng. A. 452–3 652-6
[3] Ibrahim R, Rihan R and Singh R R 2008 Eng. Fract. Mech. 75 1623-34
[4] Rihan R, Singh R R and Ibrahim R 2005 Mater. Sci. Eng. A. 407 207-12
[5] Rihan R, Singh R R and I R 2006 Int. J. Pres. Ves. Pip. 83 388-93
[6] Rihan R, Singh R R and Ibrahim R 2006 Mater. Sci. Eng. A. 425 272-7
[7] Rihan R, Singh R R and Ibrahim R 2008 Metall. Mater. Trans. A. 39 1475-8
[8] Singh R R, Rihan R and Ibrahim R 2007 Corros. Sci. 49 4386-95
[9] Pal S and Singh R R 2010 Corros. Sci. 52 1985-91
[10] Pal S, Singh R R and Rihan R 2012 Metall. Mater. Trans. A. 43A 3202-14
[11] Rihan R, Ibrahim R and Singh R R 2006 Stress corrosion cracking testing apparatus and method

Provisional Patent Registered at Watermark Patent & Trade Mark Attorneys 26th May 2006 (Australia)

[12] Rihan R, Qubbaj M, Basha M and Al-Hadhrami L 2013 Stress corrosion cracking testing device

U.S. Patent No. 8474324 B2

[13] Speidel M 1981 Metall. Mater. Trans. A. 12A 779-89
[14] Smith H, Piper D and Downey F 1968 Engng. Fract. Mech. 1 123-8
[15] Mariano N and Spinelli D 2004 Mater. Sci. Eng. A. 385 212-9
[16] Denhard E 1960 Corrosion 16 359-70
[17] Brown B and Beachem C 1965 Corros. Sci. 5 745-50
[18] Choi H, Beck F, Szklarska-Smialowska Z and Macdonald D 1982 Corrosion 38 76-85
[19] Kwon H, Wuenche A and Macdonald D 2000 Corrosion 56 482-91
[20] Fuller G and Macdonald D 1984 Corrosion 40 474-7
[21] Shim S and Szklarska-Smialowska Z 1987 Corrosion 43 286-90
[22] Shim S and Szklarska-Smialowska Z 1987 Corrosion 43 280-6
[23] Al-Mansour M, Alfantazi A and El-boujdai M 2009 Materials. Des. 30 4088-94
[24] Kisaka Y and Gerlich A 2016 Review and critical assessment of hardness criterion to avoid sulfide

stress cracking in pipeline welds ASME Pressure Vessels and Piping Conference 6B

V06BT06A023 (Vancouver, Canada)

[25] Kermani M and Harrop D 1996 The Impact of Corrosion on the Oil and Gas Industry SPE Production Facilities 186-90

[26] NACE MR0175 2003 Metals for sulfide stress cracking and stress corrosion cracking resistance

in sour oilfield environments

[27] Cui S, Li C, Wang P and Deng H 2010 J. Chin. Soc. Corr. Pro. 30 213-6
[28] Hou D, Zeng D, Shi T, Zhang Z and Deng W 2013 Pet. Sci. 10 385-94
[29] Rogne T and Edwards J 1984 Norwegian Maritime Research 12 14-23
[30] Scoppio L, Barteri M and Cumino G 1998 Metall. Ital. 90 51-9
[31] Rihan R 2017 System for testing stress corrosion cracking Patent Number: US 9541485 B1

[32] Tsujikawa S, Miyasaka A, Ueda M, Ando S, Shibata T, Haruna T, Katahira M, Yamane Y, Aoki

T and Yamada T 1993 Corrosion 49 409-19

[33] Kappes M 2011 Evaluation of thiosulphate as a substitute for hydrogen sulphide in sour corrosion

fatigue studies (Ohio, USA: The Ohio State University)

[34] Kappes M, Frankel G, Sridhar N and Carranza R 2012 J. Electrochem. Soc. 5 C195-204
[35] Townsend H 1972 Corrosion 28 39-46
[36] Rihan R, Al-Wakaa B, Tanoli N and Shalaby H 2019 J. Pet. Sci. Engng. 174 1034-41
[37] Rhodes P 1969 Corrosion 25 462-72
[38] Macdonald D, Lu P, Urquidi-Macdonald M and Yeh T 1996 Corrosion 52 768-85