Transition from Pits to Cracks in Pipeline Steel in Near-Neutral pH Solution

B. Fang[1, 2, 3, *], R.L. Eadie[2], M. Elboujdaini[4], and W. Chen[2],

1. Ross Energy Services Ltd., Calgary, AB, Canada, T2P 0W7
2. Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta, Canada, T6G 2G6
3. Environmental Corrosion Center, Institute of Metal Research, Chinese Academy of Sciences, Shenyang, China
4. CANMET Materials Technology Laboratory, 568 Booth Street, Ottawa, ON, Canada, K1A 0G1

Abstract

When pipelines fail by near-neutral pH SCC (NNpHSCC) there are usually quantities of tiny blunt cracks, frequently in crack colonies, near these failures. These small cracks are usually dormant and innocuous. The critical step in NNpHSCC failures is the process by which these cracks are able to grow in depth beyond 0.5 mm. This mechanism is far from being understood. This paper reviews our experiments to help understand the mechanisms of pit-to-crack transition and early growth from the blunt cracks.

Specimens were pitted using techniques developed in our laboratories and then cyclically loaded in near-neutral pH environment sparged with 5% CO_2 / balance N_2 gas mixture at stress ratios, strain rates and frequencies which were close to those experienced during oil pipeline operations. The conditions under which the pits become blunt cracks and under which those blunt cracks can sharpen and grow beyond 0.5 mm are reported. The changes are related to the plastic deformation near the pits for blunt cracks and the ability of the crack to concentrate hydrogen near the crack tip for crack sharpening.

1. Introduction

Near-neutral pH stress corrosion cracking (NNpHSCC) has been a significant integrity issue for gas and oil pipelines for over two decades since it was first documented in 1985 [1], and it has been investigated extensively since. More than 18,000 colonies of NNpH SCC had been reported on Canadian pipelines up to August 2000 [2], and more than 95% of these colonies became dormant. A small percentage, however, which might grow until failure if not detected and removed, would cause a considerable risk to pipeline integrity management. Between 1977 and 1996, 22 failures including 12 ruptures occurred as a direct result of NNpHSCC on Canadian pipelines [1]. Pipeline failures have been reported to decrease recently, possibly because more rigorous pipeline integrity

* Corresponding author, bfang@rossenergyservices.com

management programs have been in place. However, there still have been one or two ruptures a year in Canada since 1995 and numerous cracking discovered through ILI (in-line inspection) or hydrotesting. Although soil models and simulations have been developed to help assess risk [3], these are rather imprecise, and can only predict the occurrence of minor SCC rather than significant SCC. The mechanisms for NNpHSCC are not yet understood, and further research in this area is needed.

Generally, the main part of pipeline life is consumed in the crack initiation process. Evidence from field failures suggests that corrosion pits might be a common site for crack initiation [3]. In laboratory investigation, it has been found that the earliest cracks appeared to initiate at corrosion pits [4, 5, 6, 7] that formed around non-metallic inclusions and later cracks grew from corrosion pits that formed randomly on the surface [8, 9, 10, 11], and some cracks induced by corrosion pits were related to stress cells caused by the difference of residual stress level over a much large area [12]. These pits may act as stress raisers to initiate cracks. Cracks can also be nucleated around other types of pits associated with metallurgical discontinuities. Wang *et. al.* [13] indicated that some corrosion pits can be formed preferentially along the heavily deformed metal in scratches on the surface. It was also reported that preferential corrosion occurs at the boundaries of pearlite colonies, and transgranular crack-like features can grow from such surface attack [14]. So NNpHSCC most commonly originates from corrosion pits. When a pit is a precursor to a crack, the fundamental steps in the overall process of crack propagation may include: pit nucleation; pit propagation; pit-to-crack transition; short crack propagation and long crack propagation.

For pipelines in the field, it generally takes years for pits to grow and initiate cracks, and the pit growth may proceed under intermittent exposure conditions. Thus, it would be difficult to study NNpHSCC processes under the conditions close to those in the field. So an accelerating technique to generate pits was employed in this study, the details of which have been reported in another paper [15]. Basically it consists of an acid-immersion treatment to passivate the surface and then a second immersion in dilute hydrochloric acid, which leads to rapid pitting growth at sites where the passive layer is either removed with a needle or at innate weaknesses in the film where pits grow spontaneously.

After the transition from pits to cracks has occurred in the field, tiny, elongated blunt cracks, frequently in crack colonies, are often seen in very large numbers [16]. The vast majority of these small cracks are found to become dormant and hence tend to be innocuous. However, if the small cracks can surpass a threshold depth, around 0.5 mm [17], these cracks can be activated and begin to propagate and may eventually lead to pipeline rupture if not detected and removed. So studies concerning the growth of these small cracks and how potential growth can be identified and avoided will contribute significantly to an understanding of NNpHSCC initiation and help in pipeline integrity management.

2. Experimental

The X-52 pipeline steel specimens used in this research came from a pipe that was removed from service after more than 30 years and showed NNpHSCC colonies [18]. Pits were generated using the passivation/acid immersion method first described in [15]. After pit growth, the specimens were loaded in NNpH solution C2 (0.0274 g/L $MgSO_4 \bullet 7H_2O$, 0.0255 g/L $CaCl_2$, 0.0035 g/L KCl, 0.0195 g/L $NaHCO_3$, and 0.0606 g/L $CaCO_3$) and in aqueous soil solution (soil from a failure site of a pipeline caused by NNpHSCC in Northern Ontario—Cochrane, the ratio of the soil to distilled water was 1:5). The solutions were sparged with 5% CO_2 /balance N_2 gas mixture. One set of tests were cycled under a balanced triangular waveform with a peak normal stress of 100% of specified minimum yield strength (SMYS), a stress ratio (minimum stress/maximum stress) of 0.8, a strain rate of 6.93×10^{-8}/s, and a frequency of 1×10^{-4} Hz. Another set of tests were loaded at a stress ratio 0.63, a peak normal stress of 100% or 106% SMYS, and a frequency of 7.58×10^{-5} Hz. After loading in the solutions for six to eight months, the tests were stopped and the samples were taken out. After cleaned using EDTA and ethanol in ultrasonic cleaner, rinsing with ethanol and drying, the sample surface observations were made using optical microscopy (OM) and scanning electron microscopy (SEM). Thereafter, samples were sectioned step by step to examine crack and pit depths, and crack and pit shapes. The sectioned surfaces were perpendicular to the cracked and pitted surfaces, but along the loading directions. After each grinding and polishing step, the measurement was made using OM and SEM to reveal the crack and pit dimensions.

3. Results and discussion

3.1 Pits characteristics before NNpH SCC testing

It was clear in Figures 1a and 1b that the pits generated by using the passivation/acid-immersion method were nearly circular on surface, and semi-circular on cross-section. From these observations it can be said that the individual pits were approximately hemispherical. Hemispherical pits would arise if the growth rate on every surface were constant.

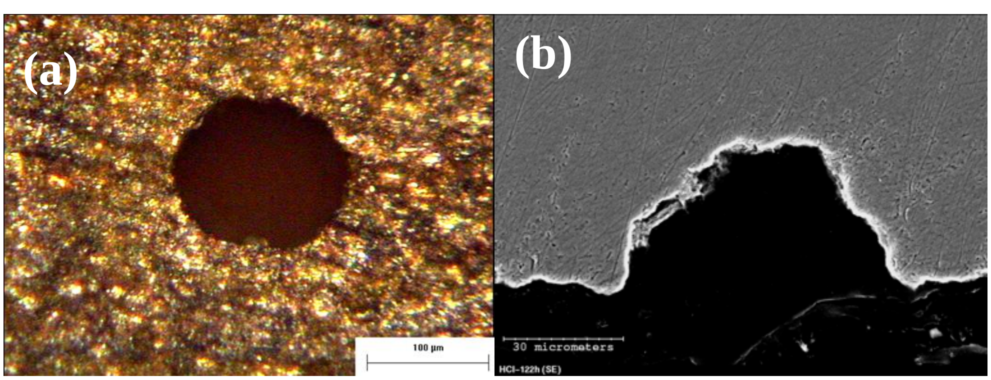


Figure 1. Pit morphologies generated using passivation/immersion technique; (a) surface view; (b) cross-section.

3.2 Blunt cracks initiation from corrosion pits

After 1345 cycles, many small blunt cracks were seen to have initiated from the bottom of pits on samples cyclically loaded in NNpH environment (Figure 2). The corrosion pits had acted as stress concentrations (micro-notches) and served to initiate the blunt flaws. The stress and deformation fields in the immediate vicinity of the corrosion pits had a strong bearing on how the NNpHSCC cracks nucleated and propagated. In the mean time, the existing pits would continue to grow during exposure by anodic dissolution. When the stress concentrations at the roots of the corrosion pits were large enough, plastic deformation would occur. Slip irreversibility was enhanced, because of the dissolution of slip steps (the anodic corrosion reaction). At the same time, the iron atoms at the surface of the plastic zone had higher energy, acting as anodes in solution compared to the relatively less deformed surrounding regions serving as cathodes. Thus, galvanic cells would form driven partly by the higher dislocation density. So preferential electrochemical attack would focus on the regions at the pits where plastic deformation was localized. Hence, dissolution in plastic zones around the corrosion pits was accelerated. This dissolution, in turn, could enhance stress concentrations. In the end, blunt cracks were initiated, as shown in Figure 2. These NNpHSCC cracks were mainly formed by stress-facilitated dissolution localized in plastic zones. Consequently, this type of crack was quite wide.

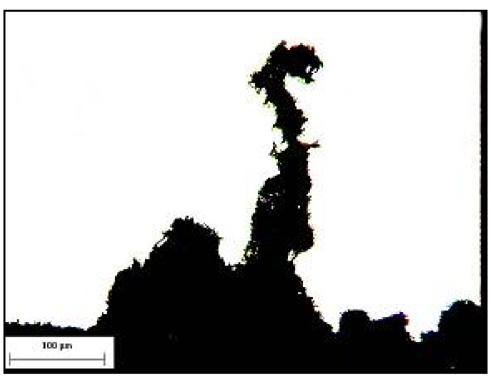
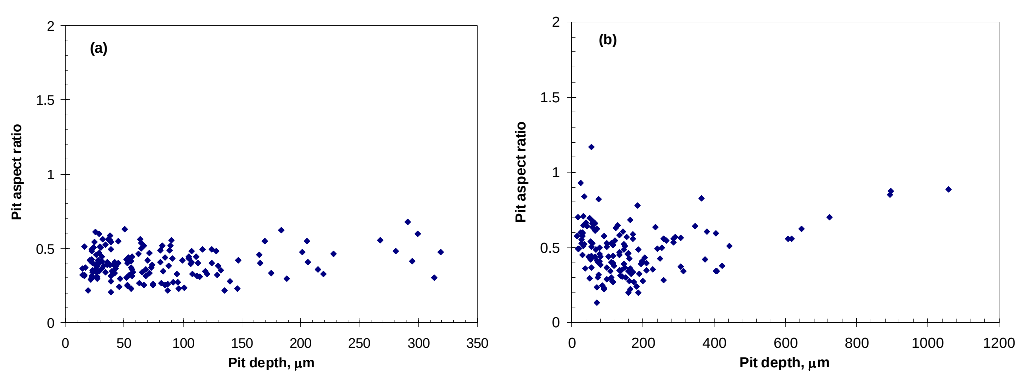


Figure 2. Photomicrograph of NNpHSCC crack cross-section feature on the R-T surface cycled in C2 solution loaded at 100% of SMYS, 0.0001 Hz and R of 0.8, showing a shallow blunt crack at the bottom of the pit

3.3 Non-cracking pits and cracking pits

When pitted samples were loaded cyclically in NNpH environment, it was found that not all of the pits were cracked. For most of non-cracking pits, the pit aspect ratios (the ratio of pit depth a to pit surface width w on that section) were below 0.6 (Figure 3a). However, many of cracking-pits were seen to have pit aspect ratios of over 0.5 (Figure 3b). This indicated that for $a/w > 0.5$, pits would likely tend to become cracks. Considering that stress concentration factor for an elliptical corrosion pit is related to *w/2a*, where *w/2* is the semi-axis which is perpendicular to the tensile loading, and *a* is the bottom radius of the corrosion pit [19], the deeper the pits, the larger the stress concentration factor. Thus, the plastic zone and the extent of surface plasticity in the corrosion pit were also larger, which would promote the dissolution of the Fe atoms within the plastic zone. When the dissolution progressed to a certain degree, the pit had become a crack. Again in Figure 3b, for the pits with aspect ratio below 0.5, the bottoms could be irregular, and the cracking locations had smaller curvature radii. Thus, the stress concentrations would be higher and cracks still tended to have initiated at the regions with higher curvature. In addition, this type of cracking is consistently found in regions of high tensile residual stress in the pipelines, where the total stress would be significantly higher than the stress just from the internal pressure in the pipeline [12, 20]. Since this was an API X-52 steel after yielding there would be some stress increase with increasing strain. Consequently, the higher degree of corrosion or cracking was believed to be primarily related to higher plastic strain. The increased plastic strain would explain the blunt cracks versus sharp cracks. This indicated that the presence of higher plastic strains ahead of the pits increased the corrosion rate. Blunt cracks initiated around many corrosion pits, which were acting as stress concentrators (micro-notches) and were the principal sites for initiation.

The ratios of crack tip width to crack mouth width for the majority of these blunt cracks were seen to be around 0.1 (Figure 3c). Thus, blunt cracks could have survived. However, this also indicated that there was significant corrosion along the crack walls. The amount of lateral corrosion significantly increased as the crack mouth was approached. It was also noted that the ratio of crack tip width/mouth width in Figure 3c was close to values seen on the same steel pipe in the field [17]. In addition, most of cracks were found to be less than 0.5 to 0.6 mm in depth, which was consistent with the observations in the field [17]. The crack morphologies observed in the tests on the samples (Figure 2) were found to be very similar to NNpHSCC cracks found in the field [17] in this pipe. So it was reasonable to say the conditions in this study could represent NNpHSCC initiation conditions encountered in the field where clusters of SCC cracks were less than 0.5 mm in depth, although the peak normal stress in this study was somewhat higher highlighting the need for high residual tensile stresses.



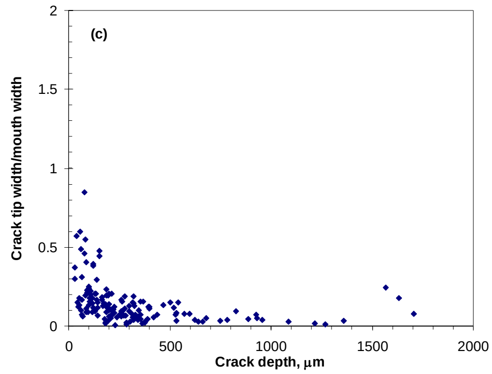


Figure 3. Geometry of pits and cracks. The aspect ratio distribution on the sample cyclically loaded at 100% of SMYS, 0.0001 Hz and R of 0.8 in NNpH solution sparged with 5% CO_2 of (a) non-cracking pits and (b) cracking pits. (c) the crack tip width/crack mouth width for cracks.

3.4 Blunt crack distribution and growth

After cyclic loading in NNpH solution, it was clearly seen that most of cracks were distributed between 30 and 390 μm in depth, as shown in Fig 4a, and the most probable crack depth was around 30 to 90 μm. Fig 4b shows that the median of crack depth was at 140 μm, and the lower and upper box values (quartiles) were 86 and 245 μm, respectively. The whisker was from 24 to 456 μm with a few outliers shown with asterisks. All the evidence once again reflected that the majority of crack depth were below 0.5 mm, consistent with the field observations.

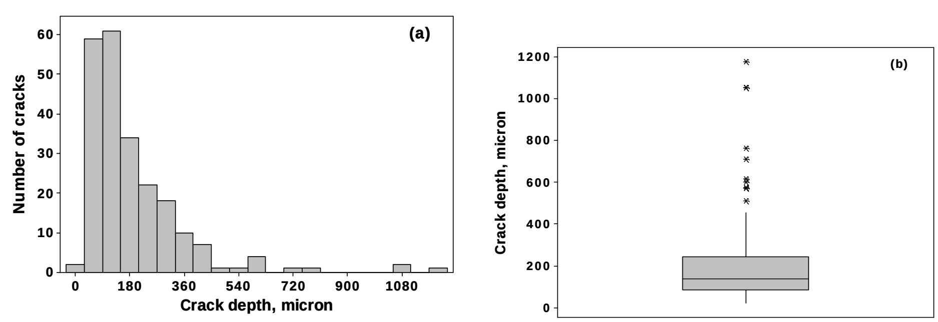


Figure 4. Distribution of crack depth on the sample cyclically loaded at 100% of SMYS, 0.0001 Hz and R of 0.8 in NNpH environment after 1345 cycles; (a) number of cracks versus crack depth; (b) boxplot of crack depth.

The blunt crack growth generated in the testing can be expressed using the Paris law. Assuming that these blunt cracks were semielliptical surface flaws with a depth of *a* and a length of 2*c*, K_I can be calculated by [21] for $a>c$:

$$K_I = (\sigma_m + H\sigma_b)\sqrt{\frac{\pi a}{Q}}F(\frac{a}{t},\frac{a}{c},\frac{c}{W},\phi) \qquad 1.1$$

where $Q = 1 + 1.464(\frac{c}{a})^{1.65}$, F is the geometric factor and other parameters are seen [21]. Thus, in the current study, the crack growth rate and cracking pits and non-cracking pits growth rates can be given in Fig 5. It was clear that the crack growth rate was higher than the non-cracking and cracking pits growth rate. This confirmed that when the crack growth rate was higher than non-cracking and cracking pits growth rates, a crack would not be dissolved and eaten away, and thus would survive. At the same time, if $\Delta K > 0.4$ MPa•m$^{1/2}$, blunt cracks could grow and survive. This is a little similar to Kondo's and Chen's models [22,23] for pit-to-crack transition. Again considering the time-based growth rate, it would be found that most of the growth rates were in a range of 10^{-9} mm/s to 10^{-8} mm/s. This growth rate is very low and should not put pipelines at a risk and thus could be considered to be dormant and hence innocuous. However, if a pipeline is expected to run for a long of time, this order of growth rate should be considered since pipelines could still eventually experience failure. The details will be discussed in the following section.

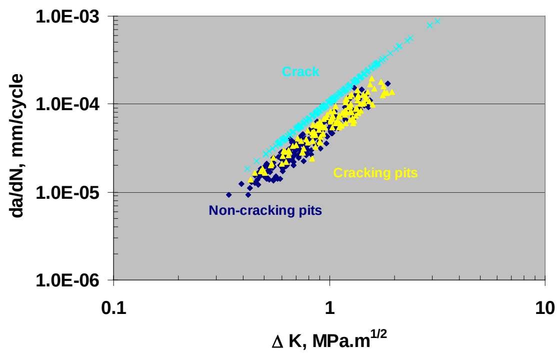


Figure 5. The growth rates for cracks, non-cracking pits and cracking pits for the sample cyclically loaded at 100% of SMYS, 0.0001 Hz and R of 0.8 in NNpH solution.

3.5 Transition from blunt crack to sharp crack and sharp crack growth

Figure 6a shows a blunt crack that had initiated from the bottom of a big pit. The blunt crack initiation and growth mechanism has been addressed above as being caused by plastic-deformation-facilitated dissolution. When blunt cracks grew deep enough, they could surpass a threshold, around 0.5 to 0.6 mm. Thereafter, the apparent dormant blunt cracks would be reactivated, and tend to start to grow. However, the morphologies of the crack tips exceeding the critical depth were significantly different from the blunt cracks. Crack tips in this stage looked very sharp, as shown in Figure 6b. Thus, anodic dissolution would not be the dominant process in this stage. When the blunt cracks grew deep enough, the plastic deformation would be larger. Thus, the corresponding plastic zones would be bigger accordingly, which would produce larger hydrostatic stress zones ahead of the deeper cracks. Hence, more hydrogen would be trapped in the larger plastic zones and could play an important role in crack growth. So, for this stage, the crack growth mechanism was hydrogen assisted cracking (HAC) instead of dissolution. In a word, there were two different mechanisms for early crack growth in NNpHSCC. Before the threshold, around 0.5 to 0.6 mm deep, referred to as “Stage I”, it was plastic-deformation-facilitated dissolution that made wide blunt crack initiation from corrosion pits and growth. After the threshold, called “Stage II”, hydrogen was responsible for the subsequent sharp crack growth. This is the first time these two different crack types have been observed and reproduced in the laboratory. These two different mechanisms are necessary for NNpHSCC crack initiation and early growth. These are quite consistent with the observations in the field. The sharp cracks in Stage II can create a significant risk to pipeline integrity. If they can’t be detected and removed, they will likely keep growing and eventually once the long crack corrosion fatigue threshold is surpassed, cracks will grow much faster, even leading to pipeline rupture or leakage. Compared to the long crack growth stage, the blunt crack growth in Stage I and the sharp crack growth in Stage II consume a majority of pipeline life. So Stages I and II cracks are very important for pipeline integrity management and should be addressed intensively. Unfortunately, so far no research has touched Stage I blunt cracks and little has paid attention to Stage II sharp cracks, while most has focused on long crack growth.

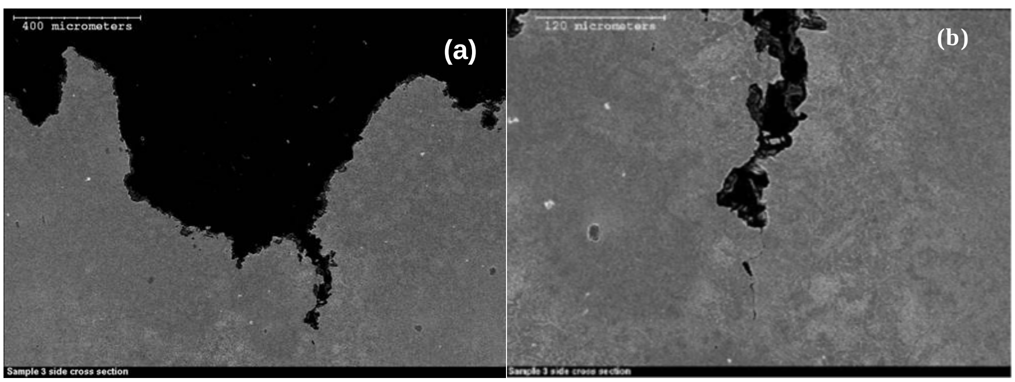


Figure 6. Photomicrographs of NNpHSCC crack cross-section feature on the R-T surface cycled in C2 solution loaded at 100% of SMYS, 0.0001 Hz and R of 0.8, showing (a) a blunt crack at the bottom of the pit; (b) a sharp crack ahead of the blunt crack.

4. Conclusions

1). The depth and the depth aspect ratio for non-cracking pits were seen to be smaller than for cracking pits. For cracking pits, generally when the pit depth aspect ratios were higher than 0.5, cracks would be likely to initiate. The deeper the pit and the higher the ratio, the higher the probability for pit-to-crack transition.

2). Blunt cracks were seen to initiate from the bottom of pits under mild cyclic loading conditions in NNpH solution, which were very close to the operational conditions. These blunt cracks were actually wide at first that were formed by plastic-deformation-facilitated dissolution, followed by sharp cracks when the depth was large enough (Stage II). The sharp cracks are believed to be associated with hydrogen, which was trapped in the tri-axial tensile zones ahead of the cracks.

3). Most of cracks were found to be shallow and wide because they tend to be dormant and not to propagate to failures. Hence, they were innocuous. Once these shallow blunt cracks exceeded a critical depth, these cracks could be activated and continue to propagate which was related to hydrogen effect. All the evidence was consistent with the field observations. Thus, the conditions employed in this research can represent the operational ones in the field, which is one of the reasons why NNpHSCC cracks have been so difficult to initiate and have not been successfully reproduced in laboratory.

5. Acknowledgements

The authors would like to acknowledge an NSERC Strategic Grant and Enbridge Pipelines Inc. for financial support, and an NSERC/AUAF facility access grant at CANMET Materials Technology Laboratory. The authors thank Scott Ironside of Enbridge for the experimental pipeline material.

6. References

[1] NEB. Stress Corrosion Cracking on Canadian Oil and Gas Pipelines. Report of the Inquiry, National Energy Board. MH-2-95. December 1996.

[2] CEPA, *CEPA* Stress Corrosion Cracking Database: Second Trending Report, August 17, 2000

[3] Michael Baker Jr., Inc., Stress Corrosion Cracking Study, TTO Number 8, Integrity Management Program Delivery Order DTRS56-020D-70036, Final Report, January 2005.

[4] B. Fang, R.L. Eadie, W. Chen, M. Elboujdaini, "Electrochemical Method Pits Generation and Its Application in Crack Initiation in Pipeline Steel in Near-Neutral pH Environment", NACE International Northern Area Western Conference "Gateway to the Oil Sands", Edmonton, Alberta, Canada, Feb. 11-14 2008.

[5] B. Fang, E.-H. Han, J. Wang, W. Ke, "Mechanical and Environmental Influences on Stress Corrosion Cracking of an X-70 Pipeline Steel in Dilute Near-Neutral pH Solutions", Corrosion 63(2007), 419-432.

[6] B. Fang, E-H Han, J.Q. Wang, W. Ke, "Influence of Strain Rate on Near-Neutral pH Environmentally Assisted Cracking of Pipeline Steels", Acta Metallurgica Sinica, 41 (2005), 1174-1182.

[7] B. Fang, E. H. Han, J.Q. Wang, W. Ke, "Stress Corrosion Cracking of X-70 Pipeline Steel in Near-Neutral pH Solution Subjected to Constant Load and

Cyclic Load Testing", Corrosion Engineering, Science and Technology, 42 (2), 123-129 (2007).

[8] Y.Z. Wang, R.W. Revie, M.R. Shehata, R.N. Parkins, and K. Krist., "Initiation of Environment Induced Cracking in Pipeline Steel: Microstructural Correlations", in Proceedings of International Pipeline Conference/1998, Vol. 1, Calgary, Canada, ASTM 1998, pp.529-542.

[9] M. Elboujdaini, Y.Z. Wang, and R.W. Revie, "Initiation of Stress Corrosion Cracking on X-65 Linepipe Steels in Near-Neutral pH Environment", in Proceedings of International Pipeline Conference/2000, Vol.2, Calgary, Canada, ASTM, 2000, pp.967-978.

[10] M. Elboujdaini, Y.Z. Wang, R.W. Revie, R.N. Parkins, and M.T. Shehata, "Stress Corrosion Crack Initiation Processes: Pitting and Microcrack Coalescence", Corrosion/2000, (Houston, TX: NACE International), 2000, Paper No.00379.

[11] Y.Z. Wang, R.W. Revie, R.N. Parkins, "Mechanistic aspects of stress corrosion crack initiation and early propagation", Corrosion/99, (Houston, TX: NACE International), 1999, Paper No.143.

[12] G. Van Boven, W. Chen, R. Rogge and R. L. Sutherby, "The Effect of Residual Stress on Pitting and Stress Corrosion Cracking of High Pressure Natural Gas Pipelines", Acta mater., **55**, pp. 29-43 (2007).

[13] S. H. Wang, W. Chen, T. Jack, F. King, R. R. Fessler, and K. Krist, "Role of Prior Cyclic Loading in the Initiation of Stress-Corrosion Cracks in Pipeline Steels Exposed to Near-Neutral pH Environment", in 2000 IPC, p.1005-1009.

[14] R. Chu, W. Chen, S. H. Wang, F. King, and R. R. Fessler, "Microstructure Dependence of Stress Corrosion Cracking Initiation in X-65 Pipeline Steel Exposed to a Near-Neutral pH Soil Environment", Corrosion, 60, p.275-283.

[15] B. Fang, R. Eadie, W. Chen, and M. Elboujdaini, "Passivation/Immersion Method to Grow Pits in Pipeline Steel and Study of Pit Nucleation and Growth Resulting from Method", Corrosion Engineering, Science and Technology, in print.

[16] W. Chen, F. King, and E. Vokes, Characteristics of Near-Neutral pH Stress Corrosion Cracks in an X-65 Pipeline, Corrosion, **58**, pp. 267-275 (2002).

[17] W. Bouaeshi, S. Ironside, and R. Eadie, "Research and Cracking Implications from an Assessment of Two Variants of Near-Neutral pH Crack Colonies in Liquid Pipelines", Corrosion, **63**(7), pp 648-660 (2007)

[18] B. Fang, R. Eadie, W. Chen, M. Elboujdaini, "Pit-To-Crack Transition in an X-52 Pipeline Steel in Near-Neutral pH Environment: I. Formation of Blunt Cracks from Pits under Cyclic Loading", Corrosion Engineering, Science and Technology, revised.

[19] W.D. Pilkey, "Peterson's Stress Concentration Factors", Second Edition, John Wiley & Sons, Inc., New York, 1997, pp.62-69.

[20] J.A. Beavers, J.T. Johnson and R.L. Sutherby, Materials Factors Influencing the Initiation of Near-Neutral pH SCC on Underground Pipelines, 2000 International Pipeline Conference, Vol. 2, pp. 979-988, New York, NY, ASME, 2000.

[21] T.L. Anderson, "Fracture Mechanics: Fundamentals and Applications", 2nd ed., Boca Raton (FL): CRC Press; 1995.

[22] Y. Kondo, "Prediction of Fatigue Crack Initiation Life Based on Pit Growth", Corrosion 45(1989) 7-11.

[23] G. S. Chen, K. C. Wan, M. Gao, R. P. Wei, T. H. Flournoy, "Transition from pitting to fatigue crack growth---modeling of corrosion fatigue crack nucleation in a 2024-T3 aluminum alloy", Materials Science and Engineering A219, 1996, p.126-132.