

Role of Hydrogen in Crack Growth in Pipeline steels Exposed to near Neutral pH Soil Environments

W. Chen¹, Richard Kania², Bob Worthingham², S. Kariyawasam²

¹ *Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Canada;*

² *TransCanada Pipelines Limited, Calgary, Canada;*

E-mail: Weixing.Chen@ualberta.ca

Abstract: This paper reports the crack growth behavior of pipeline steels in near-neutral pH environments. Crack growth data were obtained using compact tension (CT) specimens exposed to two near-neutral pH environments. The surface of CT specimens was masked either with or without coatings. The coverage of sample surface reduces the generation of hydrogen resulting from free corrosion of iron. This has caused a substantial reduction of crack growth rate and a different dependence of crack growth behavior on K_{max} , ΔK , loading frequency and environments. The growth rate data were further analyzed based on recent developed true corrosion fatigue model for pipeline steels in near neutral pH environments, from which the relative contribution of dissolution to cracking and hydrogen facilitated cracking was determined.

1 Introduction

Although it has been two decades since the first discovery of cracking of pipeline steels in near-neutral pH environments, mechanisms governing the cracking are still being debated. The cracking has been termed as stress corrosion cracking (SCC) [1-2], probably due to the fact that steel pipelines, particularly those for high-pressure gas transmission, are operated under a near static loading condition, and high pH SCC in steel pipelines can be reproduced in the laboratory under static loading [3-5]. As a result, crack growth models for pipeline steels exposed to near neutral pH soil environments are built mostly on the basis of stress corrosion cracking. Typical models that have been used include the superposition model [6, 7] and the crack tip strain rate model [7-9].

Recently, we have analyzed crack growth data both from laboratory tests using compact tension (CT) specimen and from full scale tests of shallow cracks [10, 11]. It has been found that the crack growth rate can be correlated with $\Delta K^2 K_{max}/f$ ^{α} , where ΔK is the stress intensity factor range; K_{max} is the maximum stress intensity factor; f is the loading frequency; and α is a factor related to corrosivity of soil environments. This correlation enables determination of threshold $\Delta K^2 K_{max}/f$ ^{0.1} values for long cracks such as in a test using CT specimen. The above growth correlation appears also true for small/shallow cracks in full scale

tests except that small/shallow cracks were found to grow at appreciable rates below the threshold of long cracks [11].

This investigation is aimed to understand the controlling factors on the crack growth in near-neutral pH environments on the basis of true corrosion fatigue model established. In particular, emphases will be placed on the role of hydrogen played in the growth of near neutral pH cracks in the pipeline steels.

2 Methods

An X-65 pipeline steel was used in this study, whose chemical composition (wt %) is as follows: 0.12/C, 1.5/Mn, 0.017/P, 0.0046/S, 0.26/Si, 0.014/Cu, <0.02/Ni, 0.065/Cr, <0.03/Mo, <0.01/V, 0.049/Nb, <0.005/Ti, 0.029/Al, 0.0016/Sn, 0.0012/Ca, <0.0005/B, <0.01/Pb, <0.002/Zr, and 0.004/Co. The X-65 pipeline steel was characterized to be susceptible to near-neutral pH SCC [12-14]. Compact tension (CT) specimens were machined from the X-65 pipe with the machined notch perpendicular to pipe circumferential direction. Each of the specimens was polished to produce a scratch-free surface prior to mechanical loading. The thickness of the specimen was around 9.0 ± 0.2 mm.

The machined CT specimen was pre-fatigue cracked for the initiation of a sharp crack tip from the machined notch, which was performed according to ASTM E647-93. The pre-fatigued crack length on both sides of the surface was controlled to be 2 mm to 3 mm long. The difference in crack length on both sides of the surfaces of each specimen was less than 0.2 mm.

After pre-fatigue cracking, the specimen was cyclically loaded in near-neutral pH synthetic soil solutions. A triangle waveform was used with a loading frequency in the range of 0.005 to 0.0025 Hz, a stress R-ratio of 0.6 and 0.7. The maximum and minimum stress was controlled to achieve a maximum stress intensity factor in the range of 35 to 55 $MPa\sqrt{m}$, and the stress intensity factor ranging from 10 to 28 $MPa\sqrt{m}$. The testing was performed on a pneumatic cyclic loading frame horizontally laid on bench top; the CT specimen was pin-hole loaded and sealed in the test cell with the test solution filled up to the middle of the machined notch.

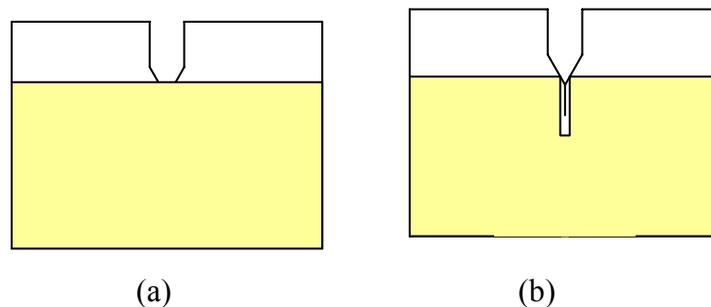


Figure 2 Schematic illustration showing coatings (shaded area) applied to the surface of CT specimens: a) complete coverage; b) partial coverage.

CT specimens in some tests were coated to prevent direct contact of soil solutions. As shown in Fig. 1, the coating was applied either to cover the entire surface (Fig. 1a), or all the surface areas except for a narrow region containing the crack. In both the cases, test solution was added to a position above the coating line.

Two types of synthetic soil solutions were used in this investigation: the NOVA Trapped Water and C2 solution [15]. Their chemical compositions are listed in Table 1. All the solutions were purged with 5% CO₂, N₂ balance to achieve a near-neutral pH value. The test solution was contained in a sealed glass cell after being purged by 5% CO₂, N₂ balance for at least 24 hours. Gas purging was also maintained during corrosion exposure.

Table 1 Chemistry of Synthetic Solutions Used in the Investigation

Chemicals	C2	NOVATW
MgSO ₄	0.0274	
CaCl ₂	0.0255	
CaCO ₃	0.0606	0.23
NaHCO ₃	0.0195	0.437
KCl	0.0035	0.015
CaSO ₄ 2H ₂ O		0.035
pH (5%CO ₂ , N ₂ balance)	6.29	7.11

Crack growth was monitored by a self-assembled potential drop system. Details of this testing system were reported in Ref [10]. The measured potential was converted to actual crack length by measuring the crack length on the fractured specimen. For the current system, the conversion factor was found to be 25.5 ± 3.5 mm/mV, which was a statistic data from a number of tests.

After corrosion exposure, the test specimen was cleaned and sectioned for examination on scanning electron microscope (SEM).

3 Results and Discussion

3.1 Competition between Crack Tip Blunting and Crack Tip Re-sharpening

The current near-neutral pH system has been characterized to produce active dissolution without the passivation of cracked surface. The active dissolution would gradually lead to crack tip blunting thus crack dormancy. Therefore, alternative process(es) must be present concurrently or sequentially to re-sharpen the crack tip in order to produce continuous growth. Such a dilemma can be best seen from the comparative tests shown in Fig. 2. In the figure, two specimens exposed to NOVATW and C2, respectively, were subjected to the same loading conditions. A hold at $35 \text{ MPa}\sqrt{m}$ for a period of about 10 days was applied to both the specimen after initial cyclic loading at $\Delta K=12 \text{ MPa}\sqrt{m}$. No crack growth was observed during the hold. However, when cyclic loading was resumed, crack growth started immediately in the specimen exposed to C2, but dormancy

remained in the specimen exposed to NOVATW. At higher K_{max} and ΔK loading, however, no dormancy in NOVATW was observed upon the restart of cyclic loading. During all the holds, no crack growth was detected, indicating the absence of stress corrosion cracking.

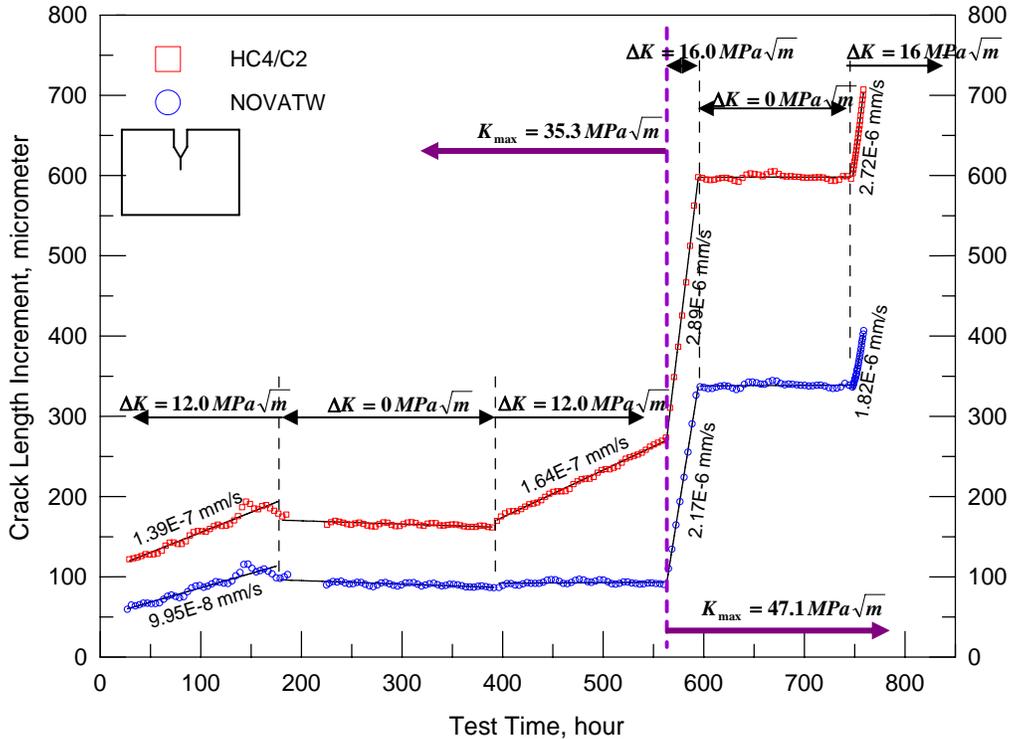


Figure 2 Crack growth as a function of test time in two different solutions.

Fig. 3 compares morphological changes at the crack tip caused by the hold at $K_{max} = 47.1 \text{ MPa}\sqrt{m}$ for about 7 days. Blunting was evident at the crack tip of both the specimens. With the low dissolution rate characteristic of NOVATW [10], blunting was likely caused by plastic deformation only, as the crack tip is broadened in a 45° direction where the shear stresses for plastic deformation are the highest. In contrast, there was massive corrosion in C2, as evidenced by the crack tip, which is blunter than that seen in NOVATW.

It was determined from weight loss experiments that the corrosion rate of pipeline steels in C2 solution was about 3 times higher than that in NOVATW [10]. This is consistent with the observation that the crack tip is blunter in the former solution. However, it was surprising that at low K_{max} and ΔK loading condition, crack growth was re-initiated in the specimen exposed to C2, which should be otherwise because of more crack tip blunting. Since the external mechanical driving force for crack growth was controlled to be the same, other factors must be considered.

It is often suspected that hydrogen may play a key role in the crack growth in near-neutral pH environments. The source of hydrogen in the current system is

primarily related to the dissolution of Fe, which generates electrons for the reduction of hydrogen ions in the system. Because of higher dissolution rate, more hydrogen atoms should be generated in C2 solution than in NOVATW.

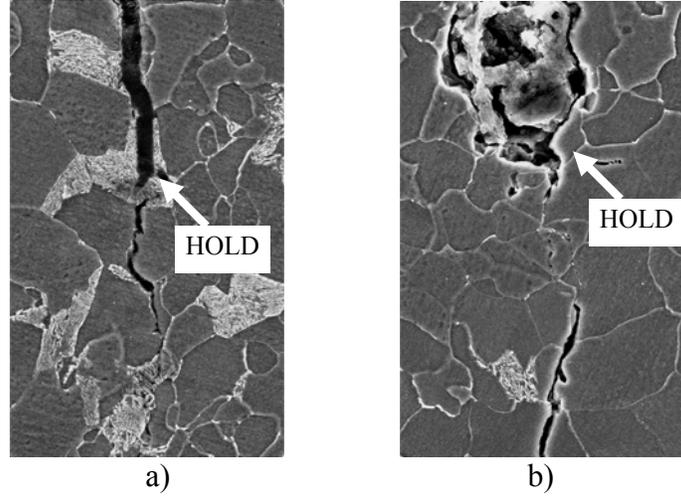


Figure 3 Crack tip morphology after a hold at constant load for 7 days in two different synthetic soil solutions: (a) in NOVATW; (b) in C2.

In the current system, hydrogen could be generated at any surfaces that were exposed to the solution. However, only the hydrogen atoms that can be segregated to the hydrostatic zone ahead of the crack tip can have any effect on crack growth. When a positive hydrostatic stress exists, hydrogen diffuses to this region in order to lower the chemical potential. Conversely, hydrogen will move out of areas that experience compressive hydrostatic stress. The equilibrium concentration of hydrogen in a stressed lattice, C_L^σ , is [16]:

$$\frac{C_L^\sigma}{C_L^0} = \exp\left(\frac{\sigma_h \bar{V}_H}{RT}\right) \quad (1)$$

Where C_L^0 is the lattice concentration of hydrogen in the absence of stress; C_L^σ is the steady state lattice concentration of hydrogen under hydrostatic stress; \bar{V}_H is the partial molar volume of hydrogen; σ_h is the hydrostatic stress; R is the universal gas constant, 8.314 J/mol·K; and T is the absolute temperature of the system.

Although corrosion at the crack tip produces hydrogen that can be diffused with a short distance to the crack tip, the segregation is related to the nominal lattice hydrogen concentration, as given in Eq. (1). Supply of hydrogen only resulted from the corrosion of crack surface in the current situation would yield limited lattice hydrogen as hydrogen atoms would diffusion down a concentration gradient to any regions with low hydrogen concentration. The surface of CT specimen is believed to be a main source of lattice hydrogen due to general

corrosion, which diffuses toward the thickness center of the CT specimen and may reach equilibrium over certain length of time depending on the diffusivity of hydrogen, test temperature and the thickness of the specimen.

3.2 Crack Growth Behavior of Coated CT Specimen

Comparative tests were performed to determine the effect of hydrogen on crack growth in near-neutral pH environments. Each set of comparative tests consisted of three specimens that were different in their surface conditions: one was with bare surfaces; the remaining two were coated with epoxy as shown in Fig. 1a) and 1b), respectively. Three tests were performed in the same environment with identical starting loading conditions: $K_{max} = 35.3 \text{ MPa}\sqrt{\text{m}}$, $\Delta K = 12.0 \text{ MPa}\sqrt{\text{m}}$, and $f = 0.005$. These loading conditions yielded a value of $(\Delta K^2 K_{max} / f^{0.1}) = 8610 \text{ MPa}^3 \text{ Hz}^{-0.1}$, which is slightly above the threshold of C2 solution ($\sim 8500 \text{ MPa}^3 \text{ Hz}^{-0.1}$), but slightly below that of NOVATW solution ($\sim 9000 \text{ MPa}^3 \text{ Hz}^{-0.1}$) [10].

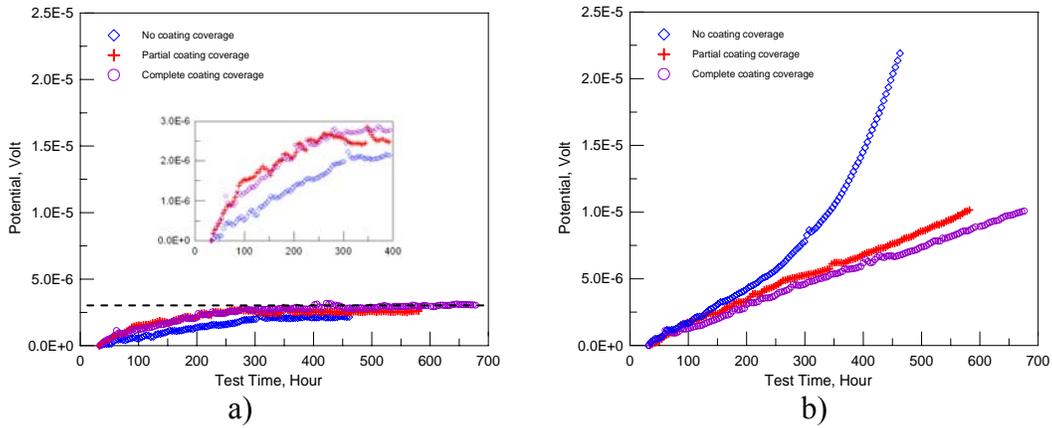


Fig. 4 Change of measured potential as a function of test time for three specimens tested in NOVATW (a) and C2 (b) solutions, respectively. All the tests were conducted at $K_{max} = 35.3 \text{ MPa}\sqrt{\text{m}}$, $\Delta K = 12.0 \text{ MPa}\sqrt{\text{m}}$, and $f = 0.005$.

As shown in Fig. 4a), the three tests in NOVATW came to a dormant state at a testing time of about 400 hours, which is consistent with the fact that the loading condition was below the threshold. In C2 solution, however, crack growth was evident, but varied significantly depending on the surface condition. Fig. 5 shows the growth rate (da/dN) as a function of testing time for all three tests in C2 solution. For the un-coated CT specimen, a three-stage process is evidenced: a growth rate nearly insensitive to testing time in the initial stage of about 275 hours, a rapid increase in growth rate in the second stage, and a reduced growth rate dependence of testing time in the third stage. For the CT specimens having epoxy-coated surfaces, the initial stage was similar to that found in the un-coated CT specimen except for a slightly lower growth rate; a decrease in growth rate was seen following the initial stage; and an increase in growth rate occurred at about 500 hours. The partially coated specimen as shown in Fig. 1b) seems to exhibit a growth behavior similar to the completed coated specimen except for a slight higher overall growth rate.

Similar tests were also conducted at a loading condition with much higher ($\Delta K^2 K_{max}/f^{0.1}$) value. Fig. 6a) shows the change of growth rate with testing time for specimens with un-coated surfaces in two different solutions. The tests at high loading conditions seemed to exhibit different growth-rate stages. The growth rate was seen to decrease with testing time in the initial stage. This is followed by a continuous increase in growth rate. The transition occurred around 275 hours seen at low loading conditions was not very obvious at high loading tests.

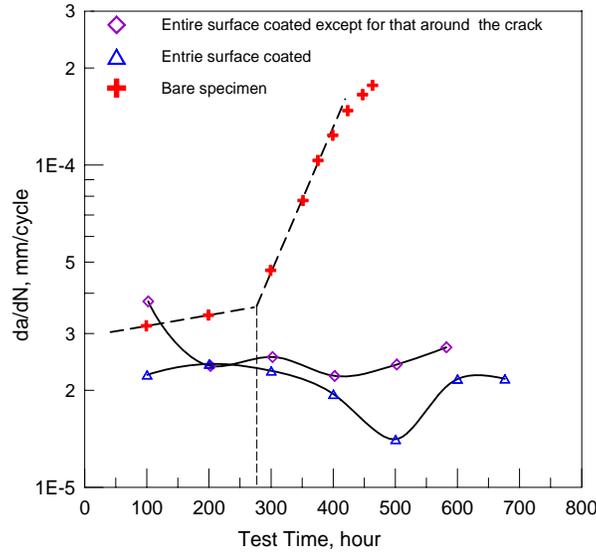


Figure 5 Crack growth rate as a function of test time for three specimens tested in C2. All the tests were conducted at $K_{max} = 35.3 \text{ MPa}\sqrt{\text{m}}$, $\Delta K = 12.0 \text{ MPa}\sqrt{\text{m}}$, and $f = 0.005$.

The above inconsistency can be understood when the effect of hydrogen is considered. As indicated previously, hydrogen generated at the surface of CT specimen is necessary to reach an equilibrium lattice hydrogen concentration in the specimen so that a high elevated hydrogen concentration can be established in the plastic zone affecting crack growth. To reach the equilibrium, a critical time of diffusion must be available. The diffusivity of hydrogen in the steel was determined to be about $2 \times 10^{-7} \text{ cm}^2/\text{s}$ [17]. For a test duration of 275 hours, this would yield a rough distance of $\sqrt{Dt} = \sqrt{2 \times 10^{-7} (\text{cm}^2/\text{s}) \times 275 \times 3600 (\text{s})} = 4.45 \text{ mm}$, which is about a half of the thickness of CT specimen used in the current investigation ($\sim 4.5 \text{ mm}$). This 275 hour test duration represents the minimum time required for hydrogen to reach the entire specimen thickness, although the peak equilibrium flux would be established at a latter time. Therefore, it is reasonable to conclude that the rapid increase in crack growth rate corresponded to the onset of hydrogen effect on crack growth.

The above critical time of hydrogen effect is not very obvious in the growth curve obtained at high loading condition. It is believed that this is caused by high growth rate due to more aggressive loading conditions. The total crack growth in the low ($\Delta K^2 K_{max}/f^{0.1}$) test (bare specimen in Fig. 5) was about 0.5 mm, which has caused a change in K_{max} and ΔK of 1.3 and 0.44 $\text{MPa}\sqrt{\text{m}}$, respectively, for the

entire test. In the transition region around 275 hour, the growth rate was very low, and K_{max} and ΔK can be assumed to be constant. The change in growth rate, therefore, is a true reflection of environmental effects on crack growth. On the other hand, the growth rate in the test with high $(\Delta K^2 K_{max}/f^{0.1})$ value represents the combined effect of environments and mechanical driving force $((\Delta K^2 K_{max}))$. As a result, the distinct effect of environments is attenuated in the growth rate curve.

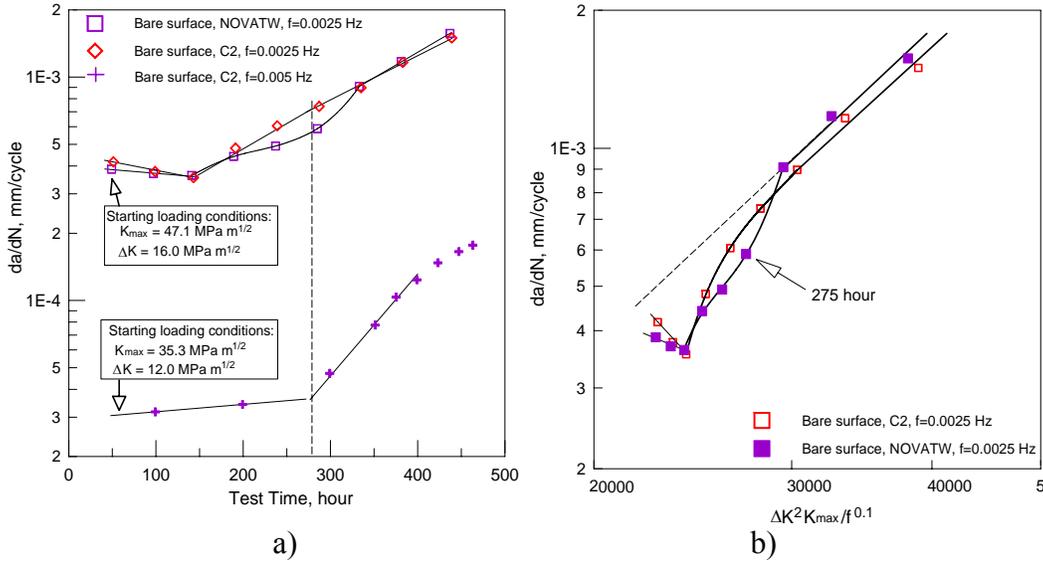


Figure 6 Crack growth rate as a function of test time a) and $\Delta K^2 K_{max}/f^{0.1}$.

When the growth data at the loading condition with high $(\Delta K^2 K_{max}/f^{0.1})$ value was normalized by $(\Delta K^2 K_{max}/f^{0.1})$, the transitional effect of hydrogen becomes clear, as shown in Fig. 6b). The curve showed an inflexion at around 275 hour, consistent with the time determined from the tests conducted at a $(\Delta K^2 K_{max}/f^{0.1})$ value near the threshold.

The above hypothesis is also consistent with the growth behavior of coated specimen loaded at high $(\Delta K^2 K_{max}/f^{0.1})$ values, as shown in Fig. 7, where the growth rate in two test solutions is presented. The growth rate of coated specimen did not show an inflexion, suggesting the transitional behavior related to hydrogen effect did not occur. The growth rate curves of coated specimen are below those of the un-coated specimens, reflecting the contribution of hydrogen on crack growth.

There was also a transitional behavior occurring at around 125 hours, below which crack growth rate was seen to decrease with increasing time. This behavior is believed to be related to morphological changes of crack tip caused by corrosion. As observed in Fig. 3, a hold at constant stress did not yield any crack growth but led to crack tip blunting through corrosion. Because of non-passivating nature of the current corrosion system, corrosion at the crack tip may contribute to the crack growth to some extent, but primarily produce general

corrosion and lead to crack tip blunting. The later would decrease the mechanical driving force for crack propagation.

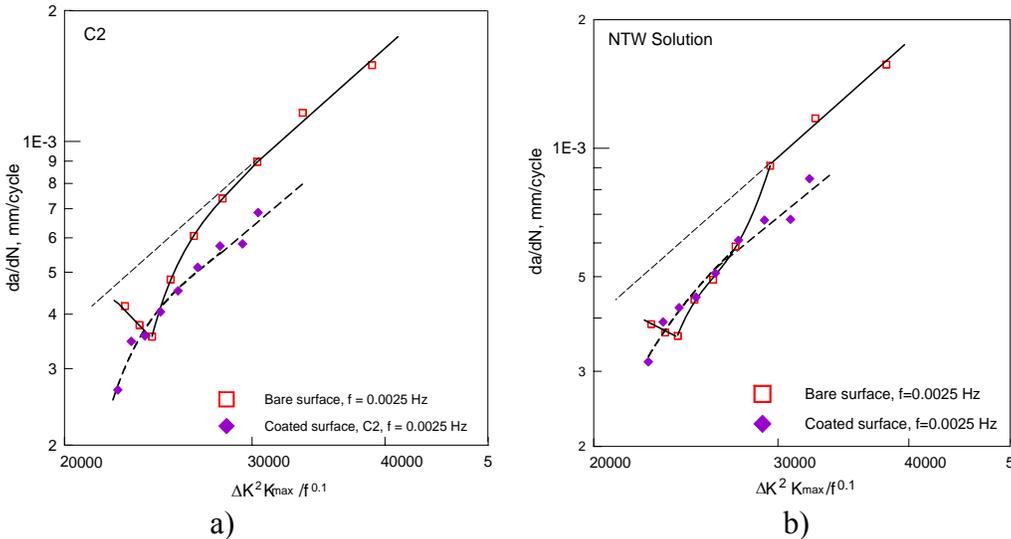


Figure 7 Comparison of crack growth behavior between bare CT specimen and the coated CT specimen: a) in C2; b) in NOVATW. All the tests were conducted with a starting $K_{max} = 47.1.3 \text{ MPa}\sqrt{\text{m}}$, $\Delta K = 16.0 \text{ MPa}\sqrt{\text{m}}$, and $f = 0.0025$.

Previous investigation has shown that the corrosion rate of near-neutral pH environments as determined by weight loss measurements was the highest at the beginning of corrosion exposure but decreases gradually to a stabilized value in about 4 days of corrosion exposure [10]. The high crack growth rate at the beginning of testing may result from higher corrosion rate of near neutral pH environments and the initial sharp crack tip from pre-fatigue cracking in air. The reduced crack growth rate reflects the fact that corrosion rate of near-neutral pH environment was decreased and crack tip became blunter due to corrosion. Crack growth rate increases as hydrogen effects become important.

When the entire surface is coated, the test solution comes in contact with the steel only through the top opening. Because the near-neutral pH condition in the current system is maintained by continuous bubbling of CO_2 through the sealed testing cell, the corrosion at the crack tip would be limited due to longer diffusion length of CO_2 gas and other corrosion species. The crack growth would be primarily determined by the mechanical driving force applied to the crack tip. As crack propagates, hydrogen generated at the crack tip may diffuse to the plastic zone and make some contribution to crack growth rate. This process maintained during the entire testing duration. As a result, only slightly lower growth rate was detected at the beginning of testing, reflecting the time required to achieve equilibrium between the generation of hydrogen at the crack tip and the diffusion of hydrogen to the plastic zone.

The above argument seems very consistent with the growth behavior observed from tests conducted at low $(\Delta K^2 K_{max} / f^{0.1})$, as shown in Fig. 5. The CT specimen

with coated surfaces (Fig. 2a) has lower growth rate than that of bare specimen, due to diffusion controlled growth phenomena as discussed before. Because of little change in mechanical driving force, the growth rate may increase slightly when hydrogen generated at the crack tip takes effect on growth rate. However, the crack growth rate should decrease gradually with increasing time due to an increased crack tip blunting. At the same time, crack growth may gradually increase the mechanical driving force, which would increase crack growth rate due to an increase in $(\Delta K^2 K_{max}/f^{0.1})$. The latter prevails after an extended test, resulting in an increase in crack growth rate as seen at about 500 hours.

3.3 Implication to the Field Observations

This investigation has clearly demonstrated the critical role of hydrogen played in the crack growth of pipeline steels exposed to near-neutral pH environments. Under a benign loading condition as determined by $(\Delta K^2 K_{max}/f^{0.1})$, near-neutral pH environments tend to blunt the crack tip through dissolution, which lead to crack dormancy as widely observed in the field. If abrupt changes in mechanical driving force are unlikely, reactivating a dormant crack is possible only when the lattice hydrogen concentration surrounding the crack tip is increased. Since hydrogen atoms are primarily generated at the external pipe surface, the lattice concentration generally decreases toward the inner surface, that is, the lattice hydrogen concentration surround the crack tip decreases as crack propagates in the depth direction. This would increase the potential of crack dormancy if mechanical driving force for crack growth is below the threshold.

There may exist many situations at which lattice hydrogen concentration surrounding the crack tip can be increased. The most influential situation may be related to an increase in cathodic protection. Other situations may include, for example, an increase of water conductivity that may extend the cathodic protection to regions with dormant cracks, an increased dissolution rate due to excessive CO₂ in the environments.

4 **Conclusions**

- 1) Corrosion/dissolution in near-neutral pH environments tends to blunt the crack tip and lead to crack dormancy.
- 2) Under a benign mechanical loading condition, crack growth rate in near-neutral pH environments is predominantly determined by the lattice hydrogen concentration surrounding the crack tip.
- 3) Although soil environments with high dissolution rate are readily to cause crack tip blunting, the hydrogen effects associated with high dissolution rate well prevail the blunting effects, particularly under a benign mechanical loading condition.
- 4) Hydrogen produced by corrosion at the crack tip is secondary in terms of crack growth as compared with hydrogen generated from pipeline surface either due to general corrosion or resulted from cathodic reaction. Near neutral pH cracks may become dormant in the depth direction simply because of the reduced lattice hydrogen concentration toward the inner

surface of the pipe. In other words, a dormant crack may be re-activated simply by an increase of lattice hydrogen concentration surrounding the crack tip.

REFERENCES:

1. B. Delanty, and J. O'Beirne, *Oil & Gas Journal*, 90, 24 (1992) 39.
2. National Energy Board, Calgary, Alberta, Canada, "Stress Corrosion Cracking on Canadian Oil & Gas Pipelines," Report # MH-2-95, Nov. 1996
3. J.M.Sutcliffe, R.R.Fessler, W.K.Boyd, R.N.Parkins, *Corrosion* 28(1972)313.
4. E. I. Meletis, *J. Mech. Behavior of Mater.* 7 (1996) 1.
5. N.Leis, R.N. Parkins, *Fatigue & Fract. Enging. Mater. & Struc.* 21(1998)583.
6. S.B. Lambert, J.A. Beavers, B. Delanty, R. Sutherby, and A. Plumtree, "Mechanical Factors Affecting Stress Corrosion Crack Growth Rates in Buried Pipelines", In *Proceedings of International Pipeline Conference*. ASME. pp. 961-966 (2000).
7. J. A. BEAVERS, "Near-Neutral pH SCC: Dormancy and Re-Initiation of Stress Corrosion Cracks", GRI report #: GRI-7045, AUGUST 2004
8. W. Zheng, W. Revie, F. A. MacLeod and O. Dinardo, "Low pH SCC: Environmental Effects on Crack propagation". Pipeline Research Council International (PRCI), July 1, 2000. Cat. No. L51791E
9. J. Been, R. Sutherby, "Effects of loading frequency on near-neutral pH crack growth on operating pipelines", *Proceedings of IPC 2006, International Pipeline Conference*, September 25-29, 2006, Calgary, Alberta, Canada.
10. W. Chen and R. L. Sutherby, *Met. & Mater. Trans A*, 38A, 1260-1268, 2007
11. W. Chen, R. Kania, R. Worthingham, S. Kariyawasam, "Crack Growth Model of Pipeline Steels in near-neutral pH Soil Environments", *Int Pipeline Conf. 2008*, paper # IPC08 64475, Calgary, Sep 29-Oct 3, 2008
12. R. Chu, W. Chen, S.-H. Wang, F. King, T. R. Jack, R. R. Fessler, *Corrosion*, 60 (3) (2004) 275.
13. W. Chen, S.-H. Wang, R. Chu, F. King, T. R. Jack, R. R. Fessler, *Metall. Mater. Trans.* 24A(2003) 2601
14. Y. Z. Wang, R. W. Revie, M. T. Shehata, in "Materials for Resource Recovery and Transport", Ed. L. Collins, The Metallurgical Society of CIM, 1998, p71.
15. W. Chen, R. L. Eadie, and R. L. Sutherby, "Environmental Effects on Near-Neutral pH Stress Corrosion Cracking in Pipelines", *Second International Conference on Environment-Induced Cracking of Metals*, September 19-23, 2004, The Banff Centre, Banff, Alberta, Canada
16. Sofronis, P. and McMeeking, R.M., Numerical Analysis of Hydrogen Transport Near a Blunting Crack, *Journal of the Mechanics and Physics of Solids* 37(3), pp. 317 – 350, (1989).
17. E. Hörnlund, J.K.T. Fossen, S. Hauger, C. Haugen, T. Havn and T. Hemmingsen, *Int. J. Electrochem. Sci.*, 2 (2007) 82 - 92