Transgranular Stress Corrosion Cracking of High-Pressure Pipelines in Contact with Solutions of Near Neutral pH

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INTRODUCTION

The majority of instances of stress corrosion cracking (SCC) in high-pressure gas pipelines has been associated with the propagation of intergranular cracks (IGSCC), but several instances of transgranular cracking (TGSCC) have been documented. TGSCC has involved service and hydrotest failures, and TGSCC frequently has been found in the region of dents in pipelines.

In those respects, TGSCC and IGSCC are identical, but the difference in crack morphology suggests that the mechanisms of growth, and therefore the conditions under which the two forms occur, are different. Since the steels involved and the operating pressures do not differ essentially for pipelines displaying the two different modes, the implication is that the different mechanisms result from variations in environmental conditions. IGSCC is associated with relatively concentrated carbonate-bicarbonate solutions with pH values in the region of 9.5. TGSCC occurs in the presence of relatively dilute solutions with pH values = 6.5. These differences in pH sometimes have prompted investigators to refer to the two forms as "high-pH" and "low-pH" cracking, although "low" is hardly applicable to solutions of pH = 6.5.

Other differences between the two modes of cracking relate to differences in environmental conditions in the broadest sense.¹ Thus, IGSCC displays a temperature sensitivity not shown by TGSCC in the field and in laboratory tests. Similarly,

ABSTRACT

Although intergranular stress corrosion cracking (IGSCC) of high-pressure gas pipelines has been known for more than 20 years, a transgranular form (TGSCC) was detected more recently. Instances of TGSCC have been associated with dilute solutions with pH values in the region of 6.5 because of the presence of carbon dioxide (CO₂). Such pH values indicate relatively little, if any, cathodic current reaches the pipe surface, since hydroxyl ions would be generated and pH would increase to values in the region of 10 if current did reach the pipe surface. Slow strain rate testing (SSRT) of pipeline steel specimens in dilute solutions of pH in the region of 6.5 suggested dissolution and hydrogen (H) ingress into the steel are involved in the crack growth mechanism. The initiation of TGSCC in specimens subjected to cyclic loading and maximum stresses approximating those of an operating line was facilitated by pitting. The geometry of the pits allowed the localized generation of solutions of lower pH than that of the bulk solution outside the pits, thereby facilitating dissolution and H discharge.

KEY WORDS: carbon dioxide, dilute solutions, hydrogen ingress, intergranular stress corrosion cracking, pH, pipelines, pitting, slow strain rate testing, steel, stress corrosion cracking, transgranular stress corrosion cracking

* Submitted for publication August 1993.
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Longitudinal weld and usually are located on only one side of the weld. The weld reinforcement probably causes the tape to bridge the immediately adjacent pipe. The void on one side of the weld is filled with adhesive, while the other side remains empty until the ingress of ground water occurs. A similar effect can occur where successive wraps of tape overlap and allow the ingress of liquid to produce a narrow strip of short cracks. A major crack may develop at the weld toe, where stress concentration or structural modification as a result of welding may facilitate crack growth. However, low-pH cracking is not invariably associated with welds, joints having an asphalt coating cracking elsewhere.

TG cracks at pipeline surfaces frequently coalesce. This issue has been studied in detail in relation to IGSCC. Crack coalescence is manifest most readily at the outer surfaces of pipes or laboratory specimens. The nearest tips of adjacent cracks pass one another before turning and growing toward one another to achieve coalescence. It is to be expected that the chances of a pair of cracks of given length interacting in this way increases as their transverse distance of separation decreases. Measurements of the transverse separations of adjacent cracks and their lengths have been made for several TGSCC colonies in pipelines. Data are shown in Figure 2 as a plot of the transverse separation against the mean length of the adjacent cracks. Those pairs of adjacent cracks that showed clear evidence of coalescence are separated from those pairs that did not by a line that defines the condition for coalescence as:

\[ y < 0.14 \] \hspace{1cm} (1)

Effects of potential on the two forms of cracking are different, as are the associated reactions and their products. For example, TGSCC often is associated with the formation of relatively large amounts of white iron carbonate between the coating and pipe surface. In IGSCC, however, the very small amount of iron carbonate that sometimes is present is incorporated in the thin magnetite films that invariably form. These films are strongly adherent to the crack sides and effectively prevent any lateral dissolution on the sides. As a result, IG cracks are narrow or fine. Conversely, the TG crack sides suffer significant lateral dissolution (Figure 1), with appreciable amounts of loosely adherent corrosion products forming in the crack enclaves. The original crack faces are destroyed, and the TG paths can be established with certainty only near the crack tip, where there has been relatively little time for dissolution of the crack sides. In contrast, the thin magnetite films that protect the IG crack sides allow the crack morphology to be retained over the whole crack length.

These differences between the two modes of cracking indicate the reactions involved in their growth are markedly different, reflecting the differences in the solutions found between pipe and coating in the vicinity of the two types of cracks. Reactions involved with IGSCC have been studied extensively, and the mechanism is understood reasonably well. However, the conditions of TGSCC have not been defined as well.

TGSCC in pipelines is characterized by very high densities of cracks in localized regions. In IGSCC, or high-pH cracking, cracks are spaced more widely. Colonies of TG cracks often are formed near a longitudinal weld and usually are located on only one side of the weld. The weld reinforcement probably causes the tape to bridge the immediately adjacent pipe. The void on one side of the weld is filled with adhesive, while the other side remains empty until the ingress of ground water occurs. A similar effect can occur where successive wraps of tape overlap and allow the ingress of liquid to produce a narrow strip of short cracks. A major crack may develop at the weld toe, where stress concentration or structural modification as a result of welding may facilitate crack growth. However, low-pH cracking is not invariably associated with welds, joints having an asphalt coating cracking elsewhere.

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\[ y < 0.14 \] \hspace{1cm} (1)
where $y$ is the transverse distance of separation and $2a$ is the mean length of the adjacent cracks. The same expression as Equation (1) has been found to hold for IGSCC in pipelines and for other steels exposed to solutions other than those to which pipelines are subject, indicating crack coalescence is related to mechanics and is not dependent upon the material or environment involved.

TGSCC colonies vary in relation to size of the colony and the maximum crack length within a colony. Together with the maximum estimated crack depth within a colony and the number of colonies per unit area, these parameters have been used to calculate a SCC severity factor for tape-coated sections of TransCanada Pipelines Co. Ltd. (TCPL) lines. That SCC severity factor has been used in conjunction with information relating to the environmental conditions along a line to identify sections where the risk of cracking appears high. This approach also has been used to identify variability in the severity of cracking in different sections when variability showed little relation to factors that influence high-pH cracking (i.e., temperature). Thus, TGSCC has been detected as far as 67 km downstream of a compressor station. In high-pH cracking, the incidence of cracking has been shown to decrease markedly with increasing distance from a compressor station so that 90% of cracking occurred within 20 km downstream of a station.

FIELD DATA

Other organizations probably have experienced TGSCC in pipelines, but TCPL has carried out extensive field investigations relating to this phenomenon. Service and hydrotest failures 15 years after installation prompted a series of investigations to obtain data on the prevalence of cracking and associated environmental circumstances. The X-65 grade pipe studied had field-applied coatings of asphalt or polyethylene tape. The incidence of cracking was appreciably greater with the polyethylene tape. About 70% of 251 excavated samples of tape-wrapped pipe, usually ~ 50 m length, revealed SCC, with an average of 11 crack colonies in each excavated sample in which cracks were discovered. By contrast, only ~ 14% of 189 excavated asphalt-coated sections showed cracks, with an average of 6.3 colonies of cracking in excavated samples found to contain cracks. The excavation locations were chosen as those most vulnerable to cracking.

At each site, the soil type and drainage pattern were determined. Location of each site was recorded with reference to its position on a slope or other features of the landscape. Data indicated cracking was significantly more prevalent, by a factor of ~ 7.5, in clays and silts (lacustrine soils) than in sands and gravels (glaciofluvial materials). A similar propensity for clays to enhance the chances of IGSCC was observed with a pipeline in Australia. In both instances, the tendency for such regions to drain poorly resulted in retention of the cracking environment and probably contributed to the enhanced cracking. Similarly, the greater density and cohesive characteristics of lacustrine soils likely enhanced the chances of coating disbondment due to soil stresses.

Data from analysis of samples of liquid collected from under coatings revealed the incidence of cracking correlated with pH, with cracking most marked when solutions of pH $\geq 6.5$ were found in the vicinity (Figure 3). The pH values may have been lower than the measured values in some cases because the liquid was effervescent in the hypodermic syringe when liquid samples were taken from between the coating and pipe. This suggested the presence of an evolving gas, most likely carbon dioxide (CO$_2$), the egress of which from the solution would have increased pH.

Figure 3 also shows low pH environments were not invariably associated with cracking. Of the liquids with pH values $\leq 7.5$, only ~ 25% were associated with cracking.

Apart from pH, the TCPL solutions were fairly dilute ground waters. Such solutions prepared in the laboratory have a pH in the vicinity of 8, but the addition of CO$_2$, which often is formed by decaying organic matter in soils, readily reduces pH to 6.5 or other values depending upon the partial pressure of the CO$_2$ in equilibrium with the solution. The retention of such low-pH liquids in the vicinity of pipe is possible only if negligible cathodic current reaches the pipe surface, since hydroxyl ions would form and pH would increase if sufficient current reached the surface.
LABORATORY TESTS WITH DILUTE SOLUTIONS CONTAINING CO₂

Experimental Methods

When TCPL first detected TGSCC, the effects of factors such as environment composition, potential, and temperature were not known. It also was not known whether TG cracks similar to those in operating pipelines could be reproduced in laboratory environments similar to those in the field. Slow strain rate testing (SSRT) was well suited to rapid surveys of the type needed initially. SSRT was conducted to encompass a range of environmental factors on samples of the X-65 steel involved in one of the joints in which TCPL experienced cracking.

The solutions used in SSRT were based upon analyses of the liquids found in the field (Table 1). It was probable that appreciable amounts of free CO₂ were present in the liquids because of the relatively large amounts of iron carbonate between coating and pipe in some regions, the most likely source of which was by reaction between solvated iron and CO₂. Consequently, SSRT was conducted in the solutions with and without CO₂. Tests were conducted at the free corrosion potential as well as at various controlled potentials and at temperatures from 5°C to 45°C. Below-ambient temperatures were achieved by pumping a cooled liquid from a refrigerated tank through plastic tubing wrapped around the outside of the cell. Above-ambient temperatures involved heating the cell with an external electrical resistance winding. Temperatures were controlled to within 1°C of the values quoted.

SSRT specimens were cut from the pipe in the longitudinal and transverse directions, although the stress corrosion responses showed no marked differences with change in orientation. Tests were conducted using cylindrical, waisted specimens 12.5 mm gauge length and 0.25 mm in diameter. Specimens were finished with 5/0 emery paper and degreased in acetone before testing. The specimens were contained in glass cells that were closed with rubber stoppers through which the ends of the specimens protruded for gripping. The cells contained facilities for bubbling gases through the solution and a probe to an external saturated calomel electrode (SCE). All potentials were quoted with respect to the SCE.

A platinum counter electrode within the cell was used for controlled potential tests, and a buffer amplifier was used for all potential measurements because of the relatively low conductivity of the dilute solutions. The strain rates applied were \(2 \times 10^{-6} \text{ s}^{-1}\). Results were considered in terms of the reduction in area (RA%) to fracture, although all specimens were examined by metallography after completion of the tests.

SSRT is a severe form of testing in that, as performed most frequently, specimens are taken monotonically to total failure. High stresses and strains usually are involved. Consequently, after SSRT was used to outline the environmental conditions likely to lead to cracking in the low-pH solutions, cyclic loading tests were performed over a range of stressing conditions down to those representative of an operating line. High maximum stresses and low R values (ratios of minimum to maximum stress) were involved in some of the tests because one objective was to determine whether relatively large cracks with morphologies identical to those in service cracks could be produced in reasonably short test times. SSRT produced rather short cracks because of the short exposure times involved. Moreover, in view of the scatter in field and SSRT data, it was anticipated that similar scatter would occur in cyclic loading tests, with scatter increasing as the maximum stress decreased. By conducting cyclic loading tests over various ranges of maximum stresses and R values, viewing the data

<table>
<thead>
<tr>
<th>Substance</th>
<th>NS1</th>
<th>NS2</th>
<th>NS3</th>
<th>NS4</th>
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<tbody>
<tr>
<td>KCl</td>
<td>0.149</td>
<td>0.142</td>
<td>0.037</td>
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<tr>
<td>NaHCO₃</td>
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<td>1.031</td>
<td>0.559</td>
<td>0.483</td>
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<tr>
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<td>0.073</td>
<td>0.008</td>
<td>0.181</td>
</tr>
<tr>
<td>MgSO₄·7H₂O</td>
<td>0.106</td>
<td>0.254</td>
<td>0.089</td>
<td>0.131</td>
</tr>
</tbody>
</table>

FIGURE 3. Numbers of liquid samples taken from below asphalt and tape coatings with pH values shown with the incidence of SCC in those locations on TCPL lines.
as a whole, and using extrapolation from the more adverse stressing conditions, it was likely that data for more realistic stressing conditions would be enhanced.

In the light of the service data and data obtained from SSRT, all of the cyclic loading tests were conducted at room temperature (RT) in the solution designated NS4 (Table 1). A mixture of CO₂ and nitrogen (N₂) was bubbled through the solution to achieve pH ≈ 6.5. Test cells were essentially the same as those used for SSRT. The majority of tests was conducted at open-circuit potential (OCP), which varied from ~ –0.60 V_SCE to –0.72 V_SCE but was mostly in the range from –0.68 V_SCE to –0.72 V_SCE. A small number of tests were carried out at the controlled potential of –0.7 V_SCE, but results were indistinguishable from those performed under OCP. Tensile specimens 12.5 mm long, 5 mm wide, and 2.5 mm thick gauge length were cut in the longitudinal direction from pipe. The outer surface of the pipe was left intact on one surface of each test specimen, and the other surfaces were ground and polished. Surface condition was important in that cracks rarely generated at polished surfaces. The original pipe surface, with the coating removed by water blasting, proved much more susceptible to crack initiation. Tests were conducted at 7.4 x 10⁻² Hz and at 3.2 x 10⁻⁴ Hz to determine whether frequency, as opposed to test time, influenced cracking. Results did not differ significantly. Specimens were subjected to cyclic loading in machines that applied weights by means of a lever system, with the cyclic component derived from the movement of a cam operating through a spring of appropriate characteristics. A load cell in the system allowed the maximum and minimum loads to be determined. Test times ranged from ~ 1 week to 3 months. At the conclusion of the tests, surfaces of the specimens were examined by scanning electron microscopy (SEM) and by optical microscopy (OM) after appropriate preparation. OM was used to determine the depth of the deepest crack. The average crack velocity was calculated by dividing the depth by the test time.

**SSRT RESULTS**

**Effects of Solution Composition and Potential**

Results from tests involving solutions NS1 through NS4 (Table 1) to which no CO₂ was added showed no major differences, although some interesting effects were observed, especially in terms of RA% as a function of potential.

Figure 4 shows plots of RA% against potential for the NS1, NS3, and NS4 solutions. The NS2 solution was used in only a few tests but with no significant differences. Although there was considerable scatter in the data, each solution displayed a similar trend in that marked reductions in RA% were apparent at potentials in the vicinity of –0.7 V_SCE, at least in several tests, followed by an increase in ductility to fracture and a

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**FIGURE 4.** Reductions in area from SSRT on X-65 steel at various potentials in three of the solutions in Table 1 and without CO₂ added. Horizontal bars refer to tests at the free corrosion potential, with the potential that persisted through most of the test indicated by the symbol at one end of the line.
further decrease as potential was lowered progressively. The intermediate potentials, at which low ductilities were observed, were a little above the pitting potential ($E_{\text{pit}}$), as measured in potentiodynamic polarization experiments, with RA% increasing from the lowest values as the potential was raised above $E_{\text{pit}}$ and dissolution became more widespread. At potentials just below $E_{\text{pit}}$, the steel behaved in a ductile manner, with RA% returning to values approaching 70% at potentials of $\approx -0.75 \text{ V}_{\text{SCE}}$. However, further reduction in potential decreased ductility, with RA% in the region of 35% at $-0.9 \text{ V}_{\text{SCE}}$. This further reduction was most probably a result of the ingress of hydrogen (H) into the steel.

Data for the longitudinal and transverse specimens in Figure 4 did not appear essentially different, although there were some indications of differences in the tendency for cracks to develop. Relatively few longitudinal specimens displayed cracks other than in the necked region, even when marked reductions in ductility were observed. However, transverse specimens developed cracks over the whole of the gauge length, although only at potentials of $\leq -0.8 \text{ V}_{\text{SCE}}$ with the NS1 and NS4 solutions, but at $\leq -0.65 \text{ V}_{\text{SCE}}$ in the NS3 solution. The significance of these differences in relation to the different solutions was not known, and they were surprising in that NS3 was the most dilute of the solutions. Nevertheless, the transverse specimens tended to develop cracks more readily than the longitudinal specimens despite no marked influence of such apparent in the RA% data.

**Effects of CO$_2$ Additions**

The effects of saturating the solutions with CO$_2$ were dramatic. RA% values obtained during SSRT were reduced markedly even at potentials ($= -0.8 \text{ V}_{\text{SCE}}$ and $-0.5 \text{ V}_{\text{SCE}}$) where Figure 4 indicated increased ductilities. Cracks also initiated over most of the gauge length of the specimens in all solutions and at most potentials, and average crack velocities were generally higher than in solutions to which no CO$_2$ was added. Figure 5 shows a plot of results for tests at RT in the various solutions saturated with CO$_2$ and involving specimens cut longitudinally and transversely from pipe material. While there again was considerable scatter, the low RA% values shown over a wide range of potentials indicated influence of the environment, since several SSRT in air all gave RA% values in the range of 70 to 75. As in tests involving solutions without CO$_2$ additions, there did not appear to be any significant difference in the behaviors of specimens cut in different orientations.

Solutions in Figure 5 had pH values $= 5.8$, which was lower than in the field data (Figure 3) for the most prevalent cracking conditions. Consequently, SSRT was conducted in solutions through which a mixture of CO$_2$ and N$_2$ was bubbled to produce pH = 6.5. Results (Figure 6) allowed comparison with trends observed for solutions without (pH = 8.2) and saturated with CO$_2$. Results for tests in solutions with pH of $\approx 6.4$ were similar to those for solutions of pH = 8.2 in that there was a significant tendency for the ductility to recover at intermediate potentials, although the data as a whole tended toward higher potentials in tests using the solution of lower pH.

Scatter in RA% values in Figures 4 through 6 might have detracted from assessing the effects of addition of CO$_2$ to the solutions. A more appropriate way to consider the data was by using Weibull plots of RA% over restricted potential ranges. Figure 7 shows
Weibull plots\(^9\) for tests in the solutions with and without CO\(_2\) saturation and for potentials in ranges including –0.65 \(V_{SCE}\) to –0.7 \(V_{SCE}\), which approximated OCP. The effect of CO\(_2\) in promoting lower ductilities at a given probability was clear for all ranges, even though above and below OCP, values were likely to be of much less significance to low-pH cracking in the field. Comparison of the plots in Figure 7 showed ductility was reduced significantly by the addition of CO\(_2\) to the solutions and by decreasing the potential. Both trends were significant indicators of the cracking mechanism.

**Effects of Temperature**

The SSRT data above related to tests at RT, but pipelines can operate above and below typical RT. Consequently, SSRT was conducted at temperatures from 5\(^\circ\)C to 45\(^\circ\)C. All of the specimens in this phase of the work were cut in the transverse direction. NS1, NS3, and NS4 solutions were involved, and different pH values were achieved by bubbling CO\(_2\) at different partial pressures through the solutions.

Figure 8 shows results from tests at various temperatures conducted in solutions of pH \(\approx 6.4\). Figure 9 shows the equivalent plot for solutions of pH \(\approx 5.8\). The lack of systematic trends in the data with temperature concurred with the field findings in which the incidence of cracking was unrelated to distance from compressor stations and, hence, to temperature.

**Fractography**

Irrespective of the exposure conditions, where relatively low ductilities were achieved in SSRT, the fracture surface invariably displayed areas of quasi-cleavage (Figure 10) such as is associated often with hydrogen-induced cracking. A further indication of the entry of H into the steel was the manifestation of secondary cracks that were not connected to the outer surface of the specimen and usually were nucleated on bands of pearlitic material (Figure 11). Nearer to the fracture surface, these cracks yawned and linked, sometimes to cracks at the outer surface, but they also were detectable in regions where lesser deformation occurred and where the yawning apparent in Figure 11 was less marked. In specimens that fractured with high RA\% values, the fracture surface invariably displayed dimples indicative of fracture propagation by microvoid coalescence, patches of which also were apparent on fracture surfaces that displayed quasi-cleavage, especially in the case of intermediate RA\% values. Cracks invariably followed TG paths, whether viewed by SEM of the fracture surface or by OM of polished and etched sections. Cracks apparent at the outer surface of the specimens contained corrosion products, except when the test potential was in the region below –0.8 \(V_{SCE}\).

**CYCLIC LOADING TEST RESULTS**

**Crack Velocities**

Most of the cyclic loading tests involved maximum stresses of 345 MPa (50 ksi), 414 MPa (60 ksi), or 483 MPa (70 ksi), with a few at 552 MPa (80 ksi) or above. The crack velocity data is plotted in Weibull form in Figure 12. As with some plots of Figure 7, the raw data did not always fall about a straight line as required by the Weibull function. This usually was because there was an incubation period before any detectable change in the measured parameter,
causing the line to be convex toward its lower end. In the present work, the sharply undulating nature of the original surface of the pipe material led to the arbitrary definition of a crack as a feature that was sharp at its tip and had a depth of 4 to 5 times the width, with a minimum depth of 0.005 mm that was measured readily at a magnification of 60x. The effect of introducing those lower boundary conditions resulted in some curvature of the line in Weibull plots. This was corrected for in the usual way by introducing the so-called location parameter (shown on each plot in Figure 12). Very few data were obtained for stresses of 552 MPa or above. Those obtained are shown in Figure 12(d). The regression line for the data was dominated by the two points at the extremes of the crack velocity range.

Clearly, in view of the few data for maximum stresses of 552 MPa or above, the result shown in Figure 12(d) was the least reliable. Even so, the maximum stress increased as the slope of the Weibull line decreased, implying that the crack velocity for a given probability increased with increasing stress, which was expected. Figure 13, derived from Figure 12, shows the 70%, 50%, 30%, 10%, and 5% chances for the average crack velocity to reach the levels shown for the various maximum stresses. This approach reflected the scatter, or element of chance, involved with this system, a fact apparent in laboratory data and in service (Figure 3). As Figure 13 indicates, two tests proceeded to total failure, but in two tests involving maximum stresses of 345 MPa and R values of 0.7 and 0.8 and in one test with a maximum stress of 620 MPa and a R value of 0.67, no cracks were detected in exposure periods lasting 1,199 h, 1,655 h, and 634 h, respectively. Moreover, the position of the abscissa in Figure 13 corresponded to the maximum allowable operating stress for a line fabricated in X-65 steel. The extrapolated lines showed crack velocity might vary by over 1 order of magnitude for that maximum stress, depending upon chance.

Multiple crack initiation in cyclic loading tests usually is indicative of corrosion playing an active role in cracking. Nevertheless, the topography of the original surface of the pipe was such that queries were raised as to whether multiple cracks could initiate under cyclic loading conditions without corrosion. Consequently, a cyclic loading test was conducted in

**FIGURE 8.** RA% from SSRT on X-65 steel in dilute solutions, through which a CO$_2$-N$_2$ mixture was bubbled to achieve pH = 6.4, conducted at various potentials and temperatures.

**FIGURE 9.** RA% from SSRT on X-65 steel in dilute solutions, through which CO$_2$ was bubbled to achieve pH = 5.8, conducted at various potentials and temperatures.

**FIGURE 10.** SEM micrograph of part of the fracture surface of SSRT specimen tested at –0.5 V$_{SCE}$ in NS1 solution saturated with CO$_2$. 
Fractography

SEM revealed cracks of various length at the surface corresponding to the original outer surface of the pipe. Cracks tended to lie within narrow bands, compared to the length over which the cracks in a group were apparent. Figure 14 shows an example with no cracks visible other than those within the band. Cracks in Figure 15 showed a similar tendency, but also indicated more readily the bending of cracks before coalescence. Measurements were made of the transverse separation and average lengths of adjacent cracks to determine whether the coalescence conditions for small cracks were similar to those for large cracks (Figure 2). The data for small cracks observed in the cyclically loaded specimens are shown in Figure 16. The line that separates the coalesced from the non-coalesced cracks indicated coalescence occurred if:

\[ y < 0.156 \]  

which was sufficiently close to the conditions in Equation (1) for large cracks to suggest that the same rule applied, irrespective of crack size. This also has been found for IGSCC of line pipe steel.3

Evidence for the coalescence of cracks also was apparent on the fracture surfaces of two cyclically loaded specimens following total failure. Figure 17 shows part of one of those fracture surfaces. Disposition of the crack arrest marks indicated at least two separately nucleated cracks coalesced in the earlier stages of growth. At higher magnification, the features of the fracture surface in Figure 17 showed very similar characteristics to those in Figure 10 from SSRT. Although derived from data from a different specimen than Figure 17, Figure 18 shows the stress corrosion fracture surface near a crack tip exposed by breaking the specimen in liquid N after completion of the cyclic loading test (compare to Figure 10). Corrosion products near the crack tip did not obscure the fracture surface, but at short distances from the tip, the fracture face was obscured by corrosion product, some of which was so loosely adherent that it was removed simply by washing. This left a blackened fracture face. The black corrosion product, most likely magnetite, had to be removed electrochemically because of its adherence. This usually revealed significant corrosion of the fracture surface, which increased as the mouth of the crack was approached.

OM was performed mostly to determine maximum crack depths. It also confirmed SEM observations of essentially TG cracks (Figure 19). Figure 19 also shows that opposite faces of the crack suffered corrosion subsequent to crack extension, since the opposing parts did not match except very near the tip.

DISCUSSION

Polarization curves for pipeline steels in the high-pH environment at a concentration that promotes IGSCC show typical active-to-passive transitions in the potential range within which cracking occurs. Such behavior was not shown by equivalent curves determined for the solutions in Table 1, whether or not CO2 was present. That difference implied a difference in the mechanism of cracking for the high- and low-pH solutions. For the high-pH solutions, crack growth was by a dissolution-controlled process, which could be modeled to give predicted velocities in good agreement with experimental measurements.2 The presence of relatively large amounts of corrosion products in low-pH cracks showed dissolution processes occurred, but polarization curves indicated the highest anodic current densities at relevant potentials were unlikely to exceed \(10^{-3} \text{ A/cm}^2\), which corresponded to a crack growth rate of \(~4 \times 10^{-9} \text{ mm/s}\) (writing Faraday's second law as a penetration rate). Such a growth rate was appreciably below the highest value determined in SSRT experiments, where velocities in excess of \(10^{-6} \text{ mm/s}\) were frequent, or in cyclic loading tests experiments involving higher maximum stresses (Figures 12[c] and [d]). Consequently, a simple dissolution model was
insufficient to explain the crack growth in low-pH solutions, although it was clear that dissolution was involved, as indicated by attack on the crack sides and by corrosion products in the crack enclave.

Pitting also may have played an important role, especially in the initiation of cracks, as exemplified by Figure 1. Moreover, the cyclic loading tests showed cracks were initiated with relative ease from the sides of specimens that displayed the original surface of the pipe compared to polished surfaces. While the undulations on the original surface provided some degree of stress concentration, that was insufficient to explain the different behaviors of the two types of surface. If so, the polished surfaces should have produced cracks at sufficiently high applied stresses, which they did not.

Conversely, when the potential was controlled a little above $E_{pit}$ during SSRT, pitting, reduced ductility, and cracks were observed sometimes. In addition, the undulations on the original pipe surfaces would constitute pre-existing pits within which the changes in solution composition that accompanied pitting reactions would be facilitated. Thus, chlorides and sulfates in the low-pH solutions could result in local acidification within pits. In turn, that acidification could facilitate some of the reactions involved in the crack growth process.

Perhaps the most significant pointer to an important component of the mechanism of crack growth in the low pH solutions was from SSRT, which showed marked reductions in the ductility to fracture at relevant potentials, especially in the presence of CO$_2$.

**FIGURE 12.** Weibull plots of the crack velocity data from cyclic loading tests on X-65 steel involving various $R$ values and maximum stresses in the ranges: (a) < 414 MPa, but mostly at 345 MPa; (b) 414 MPa to 449 MPa, but mostly at 414 MPa; (c) 483 MPa to 518 MPa, averaging 490 MPa; and (d) > 552 MPa, averaging 577 MPa.
This reduced ductility could not have been simply a consequence of the formation of cracks in the specimens, since no cracks were detected in some specimens showing a marked reduction in the ductility to fracture or the cracks were so few and small that they were unlikely to adversely influence ductility. Rather, it was most likely that a large proportion of the reduction in ductility was a result of H ingress into the steel. Figure 20 shows SSRT results for the solutions in Table 1 with or without CO$_2$ in terms of the extent of cracking over a range of potentials and pH values. The solid line represents the equilibrium potentials below which H discharge was possible. Most of the data points for tests in which cracking was observed beyond the necked region fell below that line, just as the majority of tests involving cracks solely in the neck or tests involving no cracks lie above the H line. Figure 20 also shows $E_{pit}$ for the dilute solutions with (pH = 6 to 7) or without CO$_2$ (pH = 8). Above those potentials, if pitting occurred and the potential was not so high as to promote more general corrosion, pH values of the solutions within the pits would be below those of the bulk solutions, and H discharge facilitated. That probably accounted for those data points relating to extensively cracked specimens that were above the H line in Figure 20 (i.e., those points should have been somewhere to the left of the positions shown, because the actual pH within a pit or crack would be less than the bulk solution pH used in plotting the data). The importance of CO$_2$ in cracking, displayed in Figures 6 and 7, probably was related largely to its influence in lowering pH and facilitating the discharge of H, as reflected in Figure 20 by the CO$_2$-containing solutions with pH below ~7.

Other data supported a H-related cracking mechanism for solutions with or without CO$_2$, such as the progressive shifts in the lines on Figure 7 as the potential was lowered. The internal cracking apparent in Figure 11 also would be difficult to explain without invoking a role for H. The quasi-cleavage shown in Figures 10 and 18 is typical of the fractography associated with ferritic steels exposed to H.

Field and laboratory data showed considerable scatter, with cracking not invariably occurring for...
apparently identical exposure conditions even in carefully controlled laboratory tests. There were a number of possible reasons for such scatter, beginning with the pitting process suggested as a forerunner of cracking. The stochastic nature of pitting in pipelines has received some attention from the viewpoint of pitting as a cause of failure.\textsuperscript{10} There was no reason to doubt that the scatter inherent in pitting as a cause of failure was also manifest when pitting was a forerunner of cracking. When no significant cathodic current reached the pipe surface, OCP would have been in the region of the pitting potential, but that did not mean pits would have nucleated inevitably. Even with the undulations of the original surface of the pipe facilitating pit nucleation, pits did not appear to form invariably, although they formed markedly more frequently than at polished surfaces. However, pits appeared in some specimens subjected to cyclic loading tests from which cracks did not grow. Thus, the chance occurrence of pitting was added to the chance of crack nucleation from pits, compounding the element of scatter.

Other features of the data collected from the cyclic loading tests appeared relevant to this issue. In high-pH cracking, tests similar to those reported in the present work showed a statistically significant trend for cracks to continue to nucleate with increasing test time.\textsuperscript{3} That trend plays an important role in crack growth because of its relevance to crack coalescence. While evidence for crack coalescence in low-pH cracking was readily apparent from examination of field and laboratory samples, the cyclic loading tests produced no evidence of a systematic trend for crack numbers to increase with increasing test time. In some specimens, high crack densities were observed (approaching 10 cracks per mm of section length). In other specimens, the density was markedly less for appreciably longer test times. While there was no correlation between crack density and test time, there was a very significant correlation, despite considerable scatter, between crack density and crack velocity. This correlation was not surprising in view of the evidence for crack coalescence, with increasing crack density enhancing the chances of coalescence and, thus, increasing crack velocity. Because of the stress dependence and scatter in the crack velocity data, as well as the various test times involved, the trend between crack density and velocity was most readily apparent simply from averages of those quantities for different stress levels (Table 2).

The lack of a consistent trend for crack density with time may have been related to the method used to determine the number of cracks, coupled with their tendency to occur in bands (Figures 14 and 15). Obviously, a metallographic section through such a band was likely to reveal only one or two cracks. The number of cracks in a band could have increased with time, but such a change would not have been revealed in a microsection. SEM would have been the most effective method to count cracks in a band, but the question of why cracks form in bands was of perhaps greater significance, especially from the viewpoint of eventual modeling of low-pH cracking. The distribution of IG, or high-pH, cracks approximates to randomness,\textsuperscript{11} but that did not appear to be likely with TG cracks in view of their tendency to form in bands. This
cracks. That appeared to conform with banding of the microcracks in Figures 14 and 15 and with the fracture surfaces produced by the low-pH solution. The fracture surfaces did not appear to show the markedly undulating crack fronts usually seen with high-pH cracking and that might have been a consequence of the closer spacings of the TG cracks. However, it also might have indicated that, while coalescence occurred in the early stages of the growth of TG cracks, the later stages of growth involved much less coalescence and that the later stage was dominated by the growth of an individual crack. That appears to be the case for the specimen in Figure 17, where evidence of the coalescence of a few cracks near the original surface of the pipe is apparent, but where the subsequent growth showed no evidence of further coalescence, even on those parts of the fracture surface not shown. That specimen was subjected to a very high maximum stress (552 MPa) and a low R value (0.44), and so it might have been expected that single crack growth would dominate the later stages of crack extension. However, careful examination of service cracks suggested many small, almost coplanar, cracks coalesced to produce the widest cracks and that the length of such cracks increased markedly by coalescence with further, almost coplanar cracks. It was conceivable that coalescence resulted in a long surface crack because of banding until reaching a point where the crack’s subsequent growth, especially in depth, was as a single crack.

Apart from the differences in mechanism, the largest difference from a modeling point of view was in relation to the later stages of growth, with the coalescence that plays a major role in high-pH cracking being replaced by growth of individual cracks in low-pH cracking, assuming the above speculation was valid. This proposition could be tested using the crack velocity data from Figure 12 to determine the predicted failure times for an operating line, including the element of chance incorporated in the data of that figure. It was assumed for the purposes of the calculations that a crack would need to reach a depth of 6 mm for failure to occur. Results are shown in Figure 21 as a plot of the time to failure in years against the chance of failure for various maximum stresses, although only the curve for 345 MPa (50 ksi) approached reality. That curve indicated times of the correct order for relatively low chances of failure, rising to about a 20% chance of failure in 15 y (i.e., the time to the first indications of cracking in the TCPL line). However, the estimates were based upon laboratory data from experiments in which the environmental conditions for cracking persisted and those conditions may not hold true in the field, in which case the curve for the maximum stress of 345 MPa would be moved to the right by some unknown amount.

tendency suggested sites for the nucleation of new cracks were related to the locations of existing cracks. That relation may have been a consequence of H augmenting the tendency for shear localization or instability, as indicated by the influence of H on the mixed-mode (I/III) toughness of a low-alloy steel. The relation between new cracks and existing cracks may be relevant to cracking on operating pipelines. While the distribution of those cracks often is related to the weld reinforcement causing the tape to bridge the immediately adjacent pipe, the length and straightness of some of the cracks suggested that much of the coalescence was of essentially coplanar
A further point in the context of Figure 21 concerned laboratory data and reproducibility. The maximum time used in the cyclic loading laboratory tests on which Figure 21 is based is shown on the figure. This time indicated that failure was likely only at very high stresses in such times, and even then with a rather low probability. That statement remained valid even when allowing for the thinner sections of laboratory test specimens, which would cause the curves to be moved to shorter times by a factor of 2.4. Of course, useful data may be obtained from laboratory tests interrupted before the point of failure, but the question of reproducibility remains unresolved and the necessity for replicate tests is clear.

CONCLUSIONS

- Data collected in the field showed TGSCC of high-pressure gas transmission pipelines was associated with dilute solutions with pH = 6.5. This pH region was not consistent with significant amounts of cathodic current reaching the pipe surface.
- SSRT was used to rapidly survey environment-related factors. Results showed CO₂ played an important role in the TGSCC of a grade X-65 steel. Marked reductions were seen in the ductility to fracture, even in the absence of secondary cracking, at potentials in the region of OCP.
- SSRT showed no tendency for cracking to depend upon temperature, in the range from 5°C to 45°C, in conformity with field observations.
- Cyclic loading tests over wide ranges of maximum stress and R values in solutions of pH = 6.5 produced cracking from surfaces corresponding to the original outer surface of pipe material. Those cracks had the same features observed in samples from operating lines.
- Results suggested the mechanism of TGSCC by dilute CO₂-containing solutions of pH = 6.5 involved dissolution and H ingress into the steel.
- Cracks probably initiated at pits, where a localized environment was generated that had a low enough pH to allow the discharge of H at the operative potential in the pit.
- Continuing anodic dissolution in the crack enclave is a necessary corollary to the component of crack growth resulting from H ingress, especially in the absence of appropriate applied cathodic current reaching the pipe surface. The anodic reaction is complimentary to the generation of H by the cathodic reaction.
- Some evidence from laboratory and field samples indicated the cracks formed in bands, suggesting nucleation of new cracks occurred a little beyond the tips of existing cracks.

<table>
<thead>
<tr>
<th>Maximum Stress (MPa)</th>
<th>345</th>
<th>414</th>
<th>483</th>
<th>552</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. of cracks/mm</td>
<td>1.20</td>
<td>1.86</td>
<td>1.96</td>
<td>3.93</td>
</tr>
<tr>
<td>Crack velocity 10⁻⁹ mm/s</td>
<td>7.5</td>
<td>12.1</td>
<td>66.2</td>
<td>185.5</td>
</tr>
</tbody>
</table>

(Various R values and test times not recognized in determining the averages also were involved.)
There was clear evidence from field and laboratory samples of cracks coalescing. The later stages of growth may have been dominated especially by the depthwise extension of what became a single long crack as the result of much coalescing in the earlier stages of growth.

Estimates of the lifetime of a pipe from depthwise crack velocities determined in laboratory tests and involving realistic maximum stresses gave predicted values of the correct order, but the laboratory data also indicated the chances of such a failure were not high.

Field and laboratory data showed considerable scatter, with evidence of cracking from a particular set of exposure conditions not being reproduced when those conditions were replicated. It probably is inevitable, therefore, that appropriate statistical methods will need to be involved in any approach to modeling or to the collection of laboratory data relating to TGSCC of high-pressure gas transmission pipelines.

ACKNOWLEDGMENTS

The authors acknowledge the assistance of representatives of TransCanada Pipeline Co. Ltd., who collected most the field data. Most of the laboratory data was obtained at the University of Newcastle upon Tyne for TCPL.

REFERENCES