RP3.1-10: The influence of hydrogen on the mechanical properties of X65 D

Purpose
This research was carried out to understand the hydrogen influence on the mechanical properties of pipeline steels (strength, ductility, fracture toughness) to enable an evaluation by pipeline operators of the structural integrity of natural gas pipelines if they were to transport hydrogen. The equivalent hydrogen fugacity was evaluated for the cathodic hydrogen charging conditions used to enable these results to be considered for the structural integrity evaluations.

Key findings

Strength and ductility
Linearly increasing stress tests (LISTs) were conducted for X65 D steel (representative of the Dampier to Bunbury Natural Gas Pipeline, DBNGP) in air and with cathodically generated hydrogen at 9.0 and 25.0 mA/cm^2 in 0.1 M NaOH, hydrogen charged to ensure an equilibrium hydrogen concentration throughout the specimen throughout the test:

1. Hydrogen charging had no influence on the yield strength and ultimate tensile stress (UTS) of any specimen location in the pipeline wall, including base metal, weld and heat affected zone (HAZ).
2. There was no hydrogen induced subcritical cracking (HISC), under conditions of slowly increasing stress.
3. Hydrogen charging resulted in a significant, similar reduction of ductility in specimens from the base metal, the weld metal, and the HAZ.
4. Hydrogen changed the fracture mechanism at the UTS.
5. In air, fracture started by ductile rupture in the specimen centre, followed by ductile shearing to the specimen edge.
6. With hydrogen, fracture initiated from the surface and grew by a mixture of ductile and brittle fracture.
7. These results were consistent with the literature. No subcritical cracking is expected for < X80 but HISC may occur if the hardness is high and in the HAZ for high values of the crack tip stress intensity factor.

Fracture toughness
The fracture toughness was measured for X65 D in air and with hydrogen at a sufficiently slow testing rate to allow hydrogen steady state at the crack tip:

1. The fracture toughness for the C-R orientation decreased from high values in air to ~170 MPa√m at 9, 16 and 25 mA/cm^2. These values were measured according to the ASTM E1820 standard under displacement control. The first letter in the specimen designation is the load direction normal to the fracture plane, the second letter is the direction of fracture propagation. These pipe directions are: C is circumferential, R is radial, L is longitudinal.
2. These fracture toughness values were quite high; higher than were expected from the literature.
3. The fracture toughness values in hydrogen for the L-C and C-L orientations were ~ 60% of the C-R.
4. This orientation dependence was attributed to the banded ferrite pearlite microstructure elongated in the longitudinal direction. The harder pearlite in the banded microstructure caused more crack branching and deflection for fracture propagation in the radial direction.
5. The fractography in hydrogen typically was brittle fracture with flat facets and microcracks.

Hydrogen solubility and fugacity

1. The hydrogen solubility for X65 D in equilibrium with gaseous hydrogen was evaluated from literature values and measurements using the new UQ hydrogen gas phase permeation apparatus.
2. The hydrogen fugacity was determined for cathodic hydrogen charging of X65 D, using hydrogen gas phase permeation, electrochemical hydrogen permeation, and thermal desorption spectroscopy (TDS).
3. The literature indicates that oxygen may inhibit gaseous hydrogen embrittlement.

Significance to pipeline operation

Strength and ductility (Q&A format)

What is the relation to DBNGP operation of the UQ laboratory studies?
The DBNGP has a MAOP of 8.48 MPa or 85 bar versus much higher equivalent hydrogen pressures in the testing environment at UQ. The DBNGP has a daily pressure cycle.

- Mechanical properties (strength and ductility) were measured using a slowly increasing load until fracture using the LIST (linearly increasing stress test). There was no cyclic stress in the UQ tests.
- The cathodically generated hydrogen at 9.0 mA/cm^2 was equivalent to a hydrogen pressure of 600 bar hydrogen; 25 mA/cm^2 was equivalent to 980 bar hydrogen.

What is the significance of hydrogen causing a similar reduction of ductility in specimens from the base metal, weld metal, and the HAZ?

- The ductility with hydrogen of the weld area was comparable to that of the base metal.
- That is, the weld is not a weak link in the structural integrity of the pipe.

What is the significance of hydrogen having no influence on strength?

- The hydrogen concentrations in the steel were small (0.2-0.3 wt ppm) for these testing conditions, even though the testing conditions were substantially more severe than those in pipeline service: 85 bar hydrogen in service, 600 bar or greater in the lab.
- These small hydrogen concentrations produced essentially no decrease in the strength of X65 D. Literature expectation is for little change in strength and some decrease in ductility for these hydrogen concentrations.

What is the significance that hydrogen changes the fracture mode?

- Fracture is by ductile micro-void coalescence in the absence of hydrogen.
- Hydrogen changes the fracture to a more brittle fracture mode; that is fracture is easier.
- Nevertheless, considerable energy is required for fracture initiation and propagation with hydrogen.
- Fracture occurs at the UTS with hydrogen, at a similar stress as in air.

What is significance of fracture initiation in the specimen centre in air and surface initiation with hydrogen?

- These observations would relate to fracture of a defect-free pipe stressed to stresses higher than in service, so that the applied stress causes fracture. Provided that the fracture occurs similarly to that in the mechanical testing, the fracture with hydrogen occurs at essentially the same stress, but initiates at the surface, rather than inside.
- Fracture in a tensile test in air initiates in the specimen interior because hydrostatic stresses increase inside the specimen until sufficiently large to nucleate voids typically around inclusions, which are inside the steel specimen.
- In hydrogen, hydrogen molecules dissociate at the steel surface. Atomic hydrogen dissolves in the steel, facilitates dislocation motion, and facilitates hydrogen induced fracture.
- Fracture in a tensile test with hydrogen occurs at the specimen surface because hydrogen facilitates fracture initiation. Fracture initiates at the surface because a surface crack is twice as effective as an internal crack. The stress for hydrogen crack initiation is similar to the fracture stress in air.

What is the significance of no hydrogen induced subcritical crack growth in the tensile tests?

- Fracture occurred in the UQ LISTs in the necked region of the slow tensile tests (LISTs). The neck formed at the UTS in these load-controlled tests, when the specimen became mechanically unstable and fractured.
- With hydrogen, fracture initiated from the surface, in the neck region, and only in the neck region: i.e. there was no hydrogen induced subcritical cracking for slowly increasing stress until the stress reached the UTS.
- No hydrogen induced subcritical cracking (HISC) is consistent with the literature, e.g. Kappes and Perez[1] indicated (i) no HISC in pipeline steel grades up to X80, unless there is high hardness, and (ii) there was HISC in the HAZ of pipeline steels for high applied stress intensity factors, e.g. for X60 HISC occurred for $K_{applied}$ such that: $K_{THi} = 88 \text{ MPa}\sqrt{m} < K_{applied} < \mathbf{K}_{IJH} = 117 \text{ MPa}\sqrt{m}$, where $K_{applied}$ is the applied stress intensity factor at the crack tip, K_{THi} is the threshold stress intensity factor for HISC, and K_{IJH} is the fracture toughness in hydrogen.

<u>Fracture toughness</u>

- The high values of the fracture toughness in the C-R orientation measured at UQ are supported by the orientation dependence, the microstructure dependence, and the quality of the pipe & its microstructure.
- The high fracture toughness of the X65 D steel indicates that the pipeline has a high crack tolerance.
- Pipeline operators can use these values of fracture toughness for structural integrity evaluation to evaluate critical defect size.

<u>Hydrogen solubility and fugacity</u>

- This is necessary research to support the studies on mechanical properties & fracture, identifying the hydrogen fugacity during the mechanical property evaluations, and determining the relation to service.
- The results are consistent with the literature. Research is ongoing to quantify the hydrogen solubility including in the presence of trace quantities of other gases such O_2 (see FFCRC project RP3.1-13).

ACKNOWLEDGEMENTS

<u>Researchers:</u> Md Fahdul Wahab Chowdhury [a], J Hoschke[a], M Roethig[a], J Venezuela[a], CV Tapia-Bastidas[a], Y Shu[a], L Lan [a], A Karimi[a], MB Djukic[b], T Depover[c], K Verbeken[c], Evan Grey[d], A Atrens[a,*]; [a] The University of Queensland (UQ), School of Mech and Mining Eng, St. Lucia, Qld., 4072 Australia; [b] Univ of Belgrade, Faculty of Mech Engin, Kraljice Marije 16, Belgrade 11120, Serbia; [c] Ghent Univ, Dept of Mater, Textiles and Chem Engin, Technologiepark 46, B-9052 Ghent; [d] Griffith Univ, Brisbane.

<u>Industry Advisors:</u> Tawake Rakai, Tim Aujard, Michael Jarosz, Nick Kastelein, Tom Amrein, Mehdi Fardi

Future Fuels CRC is supported through the Australian Government's Cooperative Research Centres Program. We gratefully acknowledge the cash and in-kind support from all our research, government and industry participants.

Australian Government
Department of Industry, Science and Resources

Cooperative Research Centres Program

[1] MA Kappes, T Perez, Corrosion Reviews 41 (2023) 319-3.