Report on hydrogen solubility in X65 D measured using the gas phase permeability cell

September 2024

Project number: RP3.1-13

Project title: Feasibility of the use of gas phase inhibition of hydrogen embrittlement in gas transmission pipelines carrying hydrogen

Authors: Maximillian Roethig, Andrej Atrens

Project team: Maximillian Roethig, Joshua Hoschke, Evan Gray, Clotario Tapia-Bastidas, Jeffrey Venezuela, Fahad Chowdhury, Yilei Shu, Andrej Atrens

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IMPORTANT DISCLAIMER

ACKNOWLEDGEMENT

Thanks to the researchers working on the project and our international collaborators.

PROJECT INFORMATION	
Project number	RP3-13
Project title	Oxygen inhibition of gaseous hydrogen embrittlement
Research Program	RP3: Network Lifecycle Management
Milestone Report Number	Milestone 3
Description	This milestone report describes the gas phase permeation cell and the first experimental results of the hydrogen solubility in X65 D (from the DBNGP) and the planned future experiments. The first results of the hydrogen solubility in X65 D are in good agreement with expectations from the literature and are being incorporated into a journal publication “Determination of the hydrogen fugacity during cathodic hydrogen charging of X65 D pipeline steel”.
Research Provider	The University of Queensland
Project Leader and Team	Em Prof Andrejs Atrens (UQ), Prof Evan Gray (Griffith Univ)
Industry Proponent and Advisor Team	Tawake Rakai, General Manager – Transmission Asset Management, Tim Aujard, Head of Asset Performance, Australian Gas Infrastructure Group
Related Commonwealth Schedule	RP3.1.1 Reports on the compatibility of current plastic and metallic network materials with future fuels delivered. RP3.1.2 New validated models to determine the long-term performance of materials for fuel transport delivered
Project start/completion date	**Start Date: 1 February 2022; Completion Date: 1 March 2025,** spending authorized to 12/2026 for orderly project completion because of duration of PhD program of Max Roethig
IP Access	**Restricted** – available to participants only. (It is proposed to use the text herein in journal publications).
Approved by	Tawake Rakai, General Manager – Transmission Asset Management, Tim Aujard, Head of Asset Performance, Australian Gas Infrastructure Group
Date of approval	

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Summary of Report

Hydrogen carried by gas transmission pipelines will permeate into the pipeline walls, which can lead to hydrogen embrittlement. This paper details the design of an apparatus which is being used to study the permeation of gaseous hydrogen through pipeline steels at pressures up to 17MPa and temperatures up to 200°C. The results of the permeation tests will be used to (i) characterise the diffusivity and solubility of gaseous hydrogen in pipelines, (ii) equate the conditions in hydrogen embrittlement studies which use electrochemical and gaseous hydrogen charging, and (iii) study the permeation of gaseous hydrogen blended with other gases, particularly trace amounts of oxygen. Permeation studies of hydrogen with oxygen will be used to evaluate the possible use of oxygen as an inhibitor of hydrogen embrittlement. This report describes the gas phase permeation cell and the first experimental results and the future planned experimental studies with the cell.

The first results of the hydrogen solubility in X65 D are in good agreement with expectations from the literature and are being incorporated into a journal publication “Determination of the hydrogen fugacity during cathodic hydrogen charging of X65 D pipeline steel”.

1. INTRODUCTION

The industry need is that gas transmission pipeline operators require knowledge about safe operating conditions for gas pipelines carrying hydrogen, in terms of the permissible safe operating pressure, and tolerable defect sizes. Otherwise, fractures are expected, with significant collateral damage.

This research will provide critical knowledge regarding the inhibition of hydrogen embrittlement (HE) by small amounts of added gases (O2, CH4, CO, CO2). If 100% inhibition of HE were practical, then the mechanical behaviour of the pipeline steel for a hydrogen carrying pipeline would be exactly the same as that of a gas transmission pipeline with no hydrogen and the operating characteristics would remain the same as at the present time, regardless of the hydrogen content of the gas inside the gas transmission pipeline. The use of this strategy requires in-depth understanding because thermodynamics indicates that the inhibition is a kinetic effect.

This research assesses the feasibility of the use of gas phase inhibition of environmental hydrogen embrittlement for use in gas transmission pipelines carrying hydrogen. The research proposes (i) to study the hydrogen flux entering gas transmission pipeline steels exposed to hydrogen and hydrogen methane mixtures in the presence of small amounts of added gases such as O2, CO, and CO2; and (ii) study the approach to equilibrium solubility of hydrogen in the gas transmission pipeline steels, in particular how quickly equilibrium is approached.

2. BODY OF REPORT

See attached.

3. CONCLUSIONS

The paper describes the gas phase permeability apparatus, its design, construction, assembly and first use. The first results of the hydrogen solubility in X65 D are in good agreement with expectations from the literature and are being incorporated into a journal publication “Determination of the hydrogen fugacity during cathodic hydrogen charging of X65 D pipeline steel”.

4. IMPLICATIONS AND RECOMMENDATIONS FOR INDUSTRY

This report is for noting.

5. NEXT STEP AND FUTURE WORK

The gas phase permeability cell as described in the attached paper is complete and assembled and the first experimental result are in good agreement with expectations. The next steps involve carrying out the research program as detailed above.

6. REFERENCES

(Please make sure the referencing style is consistent for all milestone reports of the project.)

Milestone M3 Report – September 2024

RP3.1-13: Feasibility of the use of gas phase inhibition of hydrogen embrittlement in gas transmission pipelines carrying hydrogen

Summary

The industry need is that gas transmission pipeline operators require knowledge of safe operating conditions for gas pipelines carrying hydrogen, in terms of the permissible safe operating pressure, and tolerable defect sizes. Otherwise, fractures could occur, with significant collateral damage.

This research aims to provide critical knowledge regarding the inhibition of gaseous hydrogen embrittlement (HE) by small amounts of added gases (e.g. O_2, CH_4, CO). If 100% inhibition of HE were practical, then the mechanical behaviour of the pipeline steel for a hydrogen carrying pipeline would be exactly the same as that of a gas transmission pipeline with no hydrogen; and the operating characteristics would remain the same as at the present time, regardless of the hydrogen content of the gas inside the gas transmission pipeline. The use of this strategy requires in-depth understanding because thermodynamics indicates that the inhibition is a kinetic effect.

The research proposes (i) to study the hydrogen flux entering a gas transmission pipeline steel exposed to hydrogen and hydrogen methane mixtures in the presence of small amounts of added gases such as O_2, CO, and CO_2; and (ii) to study the approach to the equilibrium solubility of hydrogen in the gas transmission pipeline steel, in particular how quickly equilibrium is approached.

The first results of the hydrogen solubility in X65 D (from the DBNGP) are in good agreement with expectations from the literature and are being incorporated into a journal publication "Determination of the hydrogen fugacity during cathodic hydrogen charging of X65 D pipeline steel".

The Experimental Apparatus

PERMEATION EXPERIMENTS

Hydrogen permeation experiments are used to establish the transport parameters (diffusivity, solubility, permeability) of a gas. In a typical gaseous hydrogen permeation experiment, the inlet hydrogen flux (as determined by the hydrogen pressure) is quickly increased or decreased, and the exit hydrogen flux, downstream of the investigated specimen, is recorded. The inlet flux is represented by a step function, while the exit flux resembles a sigmoid function. A single change in the inlet flux, and the corresponding change in the exit flux, is referred to as a permeation transient. Multiple transients can be performed successively to collect multiple data points for the steel's properties. Further distinction between hydrogen permeation methods can be made by the governing boundary conditions. In an ideal case, the charging condition (i.e. hydrogen pressure) remains constant and a steady-state flux is established. In contrast, in a gas phase permeation rig, a fixed volume on the downstream side of the permeation membrane results in downstream pressure increasing somewhat over time, and a fixed upstream volume results in a somewhat decreasing upstream pressure. This causes the flux to be in a transient state throughout the experiment. However, this effect is expected to be small for the gas volumes used in this apparatus. This proposed hydrogen permeation apparatus (HPA) uses high-pressure hydrogen gas charging, closely replicating the pressures expected in gas pipelines carrying hydrogen. The approach enables the study of the influence of different hydrogen gas blends and added impurities by injection of the proposed gas phase inhibitors. Finally, gas phase permeation allows the determination of the hydrogen solubility in the steel membrane as a function of the hydrogen partial pressure.

DESIGN

The hydrogen permeation apparatus (HPA) was built to measure the transport parameters (diffusivity, solubility, permeability) of gaseous hydrogen through a pipeline steel. The HPA is assembled in the National Hydrogen Materials Reference Facility (NHMRF) at Griffith University, under the direction of Prof. Evan Gray.

A schematic piping and instrumentation diagram (P&ID) is depicted in Figure 1. The working principle is as

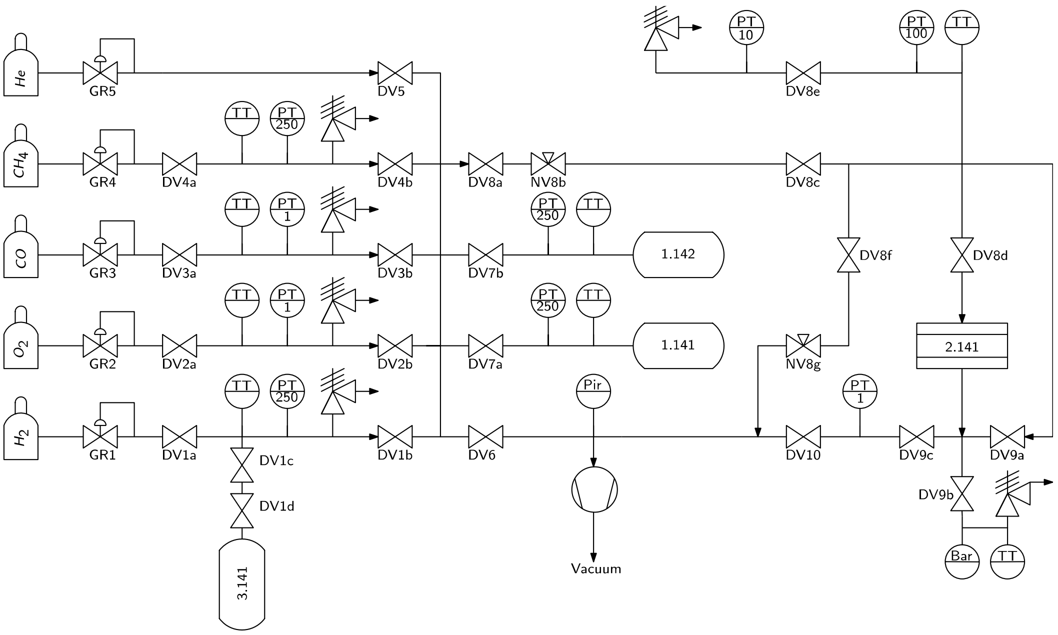


Figure 1 Schematic P&ID of the HPA.

follows. A metal hydride compressor (3.141 in Figure 1) charges extra-high purity hydrogen into the system. The hydrogen is stored in one or both sample cylinders (1.141, 1.142), depending on the type of experiment. From there, pure hydrogen permeation experiments can be started or proposed inhibitor gases may be charged into the system to establish gas mixtures to be investigated. The permeation cell (2.141 in Figure 1) is loaded with a disc specimen (diameter 32 mm, thickness 4 mm) of the pipeline steel to be investigated. The established high-pressure hydrogen or gas mixture of hydrogen and inhibitor gas is charged from the sample cylinders (1.141, 1.142) to upstream of the permeation cell. Downstream of the permeation cell, a rotary vane pump is used to create a rough vacuum (approximately 0.08 mbar). A low-pressure transducer (Baratron AA04A, full scale 13 mbar) is used to measure the minute pressure increase due to the hydrogen permeation through the disc specimen. This pressure increase over time can be converted to a hydrogen flux which can further be analysed to calculate the transport parameters of hydrogen through the investigated steel by deploying appropriate diffusion models. Furthermore, the permeation cell is equipped with a band heater. This allows for activation of the specimen by heating up to 200 °C in conjunction with hydrogen charging from both upstream and downstream. Activation is expected to remove the surface oxide layer and to fill deep traps that may influence simple diffusion models. In a subsequent step, heating in conjunction with established vacuum upstream and downstream of the specimen may release captured hydrogen in traps. This could be used to evaluate trapping parameters in a later stage of the project.

DATA ANALYSIS

A calculation spreadsheet was developed to solve the equation of state of the employed gases at the measured pressure and temperature. The calculations make use of the software REFPROP (Reference Fluid Thermodynamic and Transport Properties Database) from the National Institute of Standards and Technology (NIST). With this spreadsheet it is also possible to calculate the amount of substance based on the calibrated volume, the pressure, and the temperature reading. Furthermore, the spreadsheet was used to estimate the required sizes of the sample cylinders to store enough gas to enable rise and decay permeation transients and to establish the desired gas mixtures.

The permeation flux is given by

$$J(t) = \frac{dn}{dt}\frac{1}{A}$$

where *n* is the amount of hydrogen, *t* is time, and *A* is the area from which hydrogen is egressing. If the boundary conditions are that of constant hydrogen concentration on the upstream side, and zero hydrogen concentration on the downstream side, the flux is expected to be given by

$$\frac{J_t - J_0}{J_\infty - J_0} = \frac{2L}{\sqrt{\pi D t}} \sum_{n=0}^{\infty} exp\left(-\frac{(2n+1)^2 L^2}{4Dt}\right)$$

where J_0 is the flux before the transient (in this case 0), J_∞ is the steady-state value which the flux approaches, *L* is the thickness of the specimen, *t* is the time since the transient began, and *D* is the diffusion coefficient. The pressure, *P*, in the downstream chamber is related to the flux by

$$\frac{dP}{dt} = J(t)\frac{AZRT}{V}$$

where *R* is the gas constant, *Z* is the compressibility factor, *T* is the temperature, and *V* is the downstream volume. Combining both equations gives:

$$\frac{\left(\frac{dp}{dt}\right)_t - \left(\frac{dp}{dt}\right)_0}{\left(\frac{dp}{dt}\right)_\infty - \left(\frac{dp}{dt}\right)_0} = \frac{AZRT}{V}\frac{2L}{\sqrt{\pi D t}} \sum_{n=0}^{\infty} exp\left(-\frac{(2n+1)^2 L^2}{4Dt}\right)$$

Fitting the shape of this theoretical pressure transient to the experimentally measured time derivative of the pressure enables measurement of the effective diffusion coefficient of the steel. Using the effective diffusion coefficient *D* and the attained steady-state flux J_∞, the equilibrium hydrogen concentration c_H on the entry side of the specimen can be calculated based on Fick's first law:

$$c_H = \frac{J_\infty L}{D}$$

Furthermore, using Sieverts' law

$$c_H = S\sqrt{p}$$

Fick's first law can be rewritten to give the permeability of hydrogen through the investigated sample:

$$\Phi = J_\infty \frac{L}{\sqrt{p}}$$

Then, using the relationship

$$\Phi = DS$$

the equilibrium solubility *S* of hydrogen can be calculated.

Results

HYDROGEN DIFFUSIVITY, SOLUBILITY AND PERMEABILITY IN X65 AT ROOM TEMPERATURE

Figure 2 depicts a typical rise transient. At the start of an experiment the exit volume that is connected to the vacuum gauge is evacuated to a sufficiently low vacuum level. Next, the volume upstream of the permeation cell is charged with hydrogen at a distinct pressure. This pressure causes a small measurable pressure rise in the exit volume downstream of the permeation specimen, measured by the vacuum gauge. The experimental data to date, using pure hydrogen, are summarised in Table 1.

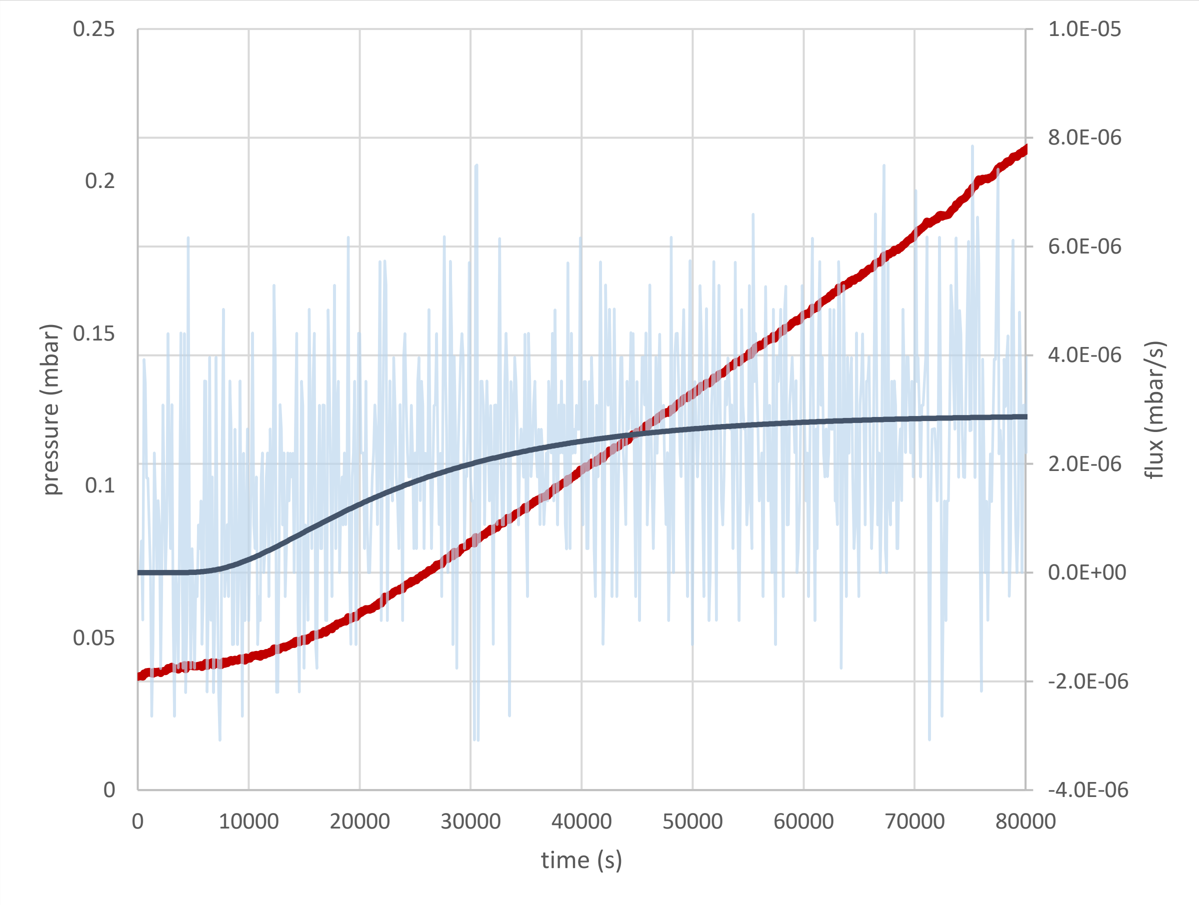


Figure 2 Measured pressure increase (red) and calculated flux (light blue) over time. The Laplace solution to Fick's second law with the appropriate boundary conditions was fitted to the experimental data (dark blue).

Table 1 Summary of the experimental data at UQ and literature values for comparison.

Author	Steel	Gas & p_H	D_{eff} (cm2/s)	S_{eff} (wppm/√bar)	CH (wppm)	√*f* (√bar)	Run	Ref.
UQ	**X65**	**H2 41.1 bar**	**1.2**	**0.0180**	**0.116**	**6.5**	**1.1**	
	X65	**H2 26.9 bar**	**1.2**	**0.0132**	**0.069**	**5.2**	**2.1**	
	X65	**H2 39.9 bar**	**1.2**	**0.0153**	**0.097**	**6.4**	**2.2**	
	X65	**H2 12.5 bar**	**1.1**	**0.0129**	**0.0458**	**3.5**	**3.1**	
	X65	**H2 21.9 bar**	**1.1**	**0.0144**	**0.0676**	**4.7**	**3.2**	
	X65	**H2 21.9 bar**	**1.1**	**0.0166**	**0.1065**	**6.4**	**3.3**	
Koren	X65 V	H2 10 bar	1.6	0.0125	0.047	3.2		[1]
	X65 V	H2 50 bar	1.6	0.0125	0.082	7.2		
	X65 V	H2 100 bar	1.6	0.0125	0.137	10.3		
Koren	X65 M	H2 10 bar	2.3	0.009	0.031	3.2		[2]
	X65 M	H2 50 bar	2.3	0.009	0.066	7.2		
	X65 M	H2 100 bar	2.3	0.009	0.095	10.3		
Xu	X52	H2 20 bar	1.6	0.0194	0.087	4.5		[3]
	X52	H2 1 bar	1.6	0.0194	0.019	1		

Using the above equations, the hydrogen flux through the specimen that is proportional to the derivative of the pressure curve, Figure 2, was fitted to obtain the specimen's transport parameters diffusivity and solubility. The results are compiled in Table 1 and graphed in Figure 3.

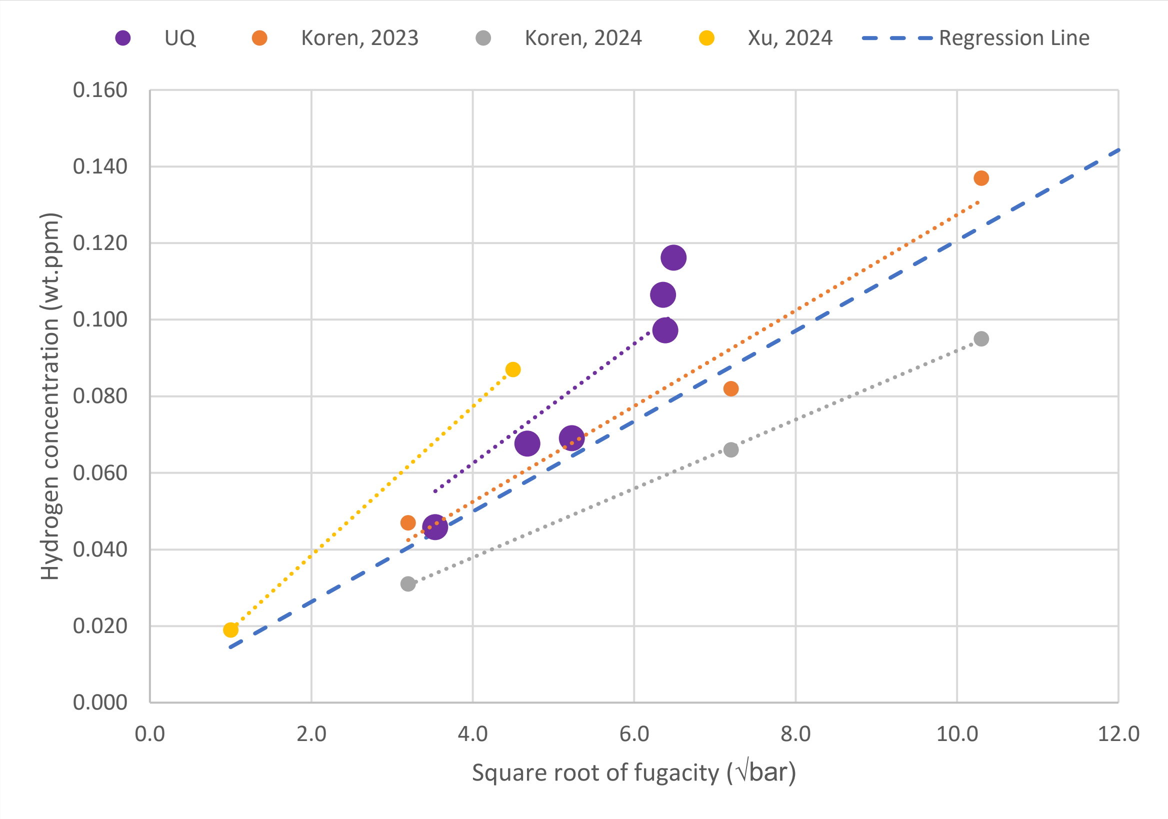
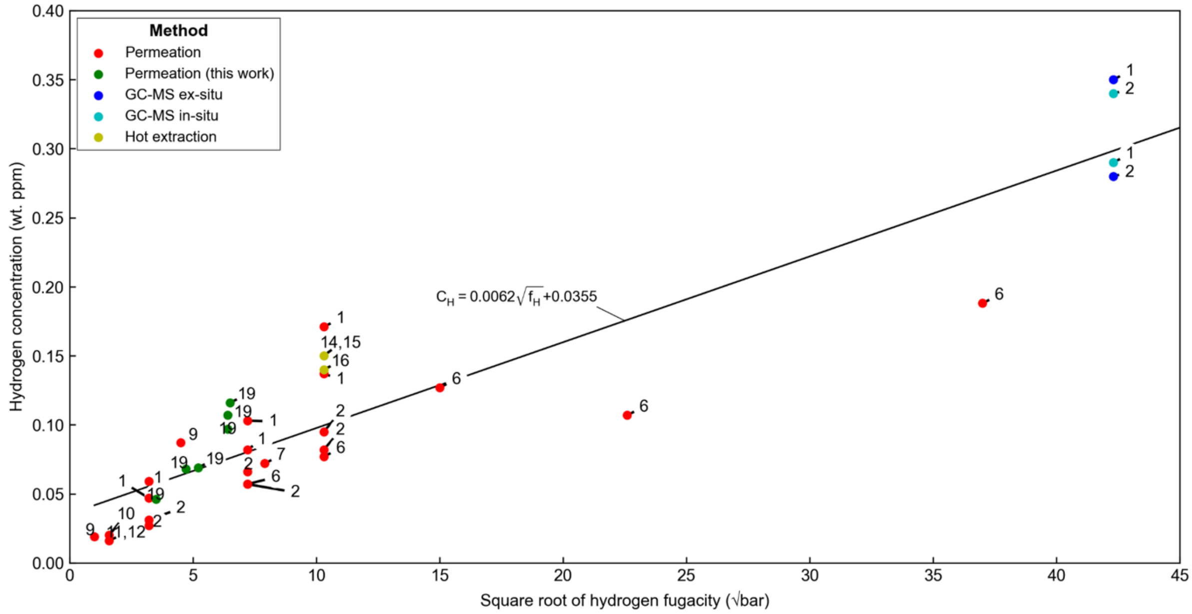


Figure 3 Hydrogen content for X65 pipeline steel against square root of hydrogen fugacity for exposure to high-pressure hydrogen gas.

The measurements are comparable to recent publications from Koren et al. [1], [2] and Xu et al. [3]. The solubilities listed in Table 1 were calculated based on Sieverts' law for each individual experiment. Furthermore, a linear regression line (purple dotted) gives the global solubility with 0.0219 wppm/√bar. Forcing the regression line through the origin yields a solubility of 0.0156 wppm/√bar that more closely resembles the individually calculated solubilities and the literature values. Fig. 4 is from the paper in preparation for publication, which plots the hydrogen concentration in equilibrium with hydrogen gas as characterized by the hydrogen fugacity. The data from this work are indicated as from this work.



Steel and first author

1	X65 V Koren	7	X52 Zhou	11,12	X80 WM & CGHAZ Zhao	16	X70 Golisch
2	X65 M Koren	9	X52 Xu	14,15	X52M & X52N Golisch	19	X65 D This work
6	X65 SMLS Ishikawa	10	X80 BM Zhao				

Fig. 4 The hydrogen concentration in X65 in equilibrium with hydrogen gas as characterized by the hydrogen fugacity. The data from this work are indicated as from this work.

Research Timeline

The next steps to completion are:

Task	**Target**
- Order gas cylinders for oxygen and methane - Purchase initiated; awaiting approval from the Griffith University safety manager.	ongoing
- Correlate analysed data from the gaseous permeation experiments using X65 steel with Joshua's electrochemical permeation experiments. This establishes the relationship between hydrogen charging pressure and concentration. - Paper draft with Josh: "Hydrogen Fugacity for Cathodic Hydrogen Charging in an X65 Gas Pipeline Steel"	ongoing
- Update the design of the permeation cell to produce a new one that will be rated for higher pressures. Also, the sealing should be updated to allow the use of bigger O-rings that likely lead to better sealing.	ongoing
- Commission the new permeation cell.	ongoing
- Further gas permeation experiments with pure hydrogen at various pressures. - Refine the data analysis, implementing direct pressure curve-fitting.	ongoing

- Connect the metal hydride sample cylinder to the apparatus. With that setup we will be able to achieve higher pressures than with just using the compressed hydrogen gas cylinder.	End of 2024
- Start experiments using high-pressure hydrogen containing proposed inhibitor gases. - Paper draft in 2025: "On the inhibition of hydrogen entry and permeation through X65 pipeline steel by the presence of added oxygen using the gas phase charging"	End Nov 2024
- Use other pipeline steels (X52, X70, X42) to get baseline results in pure hydrogen. - Run gas phase inhibition experiments on those steels to compare to X65. - Further testing of the robustness of gaseous inhibition by injection of the inhibitor gas at different times during the experiment. - Paper draft	2025
- Analyse permeation data based on different models, including reversible and irreversible trapping. - (Paper draft?)	2025
- More extensive experiments using different added gases (potentially CO) in different concentrations (10 – 1000 ppm). - (Paper draft?)	2025

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[1] E. Koren, C. M. H. Hagen, D. Wang, X. Lu, R. Johnsen, and J. Yamabe, "Experimental comparison of gaseous and electrochemical hydrogen charging in X65 pipeline steel using the permeation technique," *Corros. Sci.*, vol. 215, p. 111025, May 2023, doi: 10.1016/j.corsci.2023.111025.

[2] E. Koren, J. Yamabe, X. Lu, C. M. H. Hagen, D. Wang, and R. Johnsen, "Hydrogen diffusivity in X65 pipeline steel: Desorption and permeation studies," *Int. J. Hydrog. Energy*, vol. 61, pp. 1157–1169, Apr. 2024, doi: 10.1016/j.ijhydene.2024.03.027.

[3] X. Xu, R. Zhang, C. Wang, C. Liu, J. Zhang, and Y. Li, "Experimental study on the temperature dependence of gaseous hydrogen permeation and hydrogen embrittlement susceptibility of X52 pipeline steel," *Eng. Fail. Anal.*, vol. 155, p. 107746, Jan. 2024, doi: 10.1016/j.engfailanal.2023.107746.

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www.futurefuelscrc.com

info@futurefuelscrc.com

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