Report on "Literature Survey on Repurposing Pipelines for Hydrogen Service"

for

Project #978: on "Determining the Required Modifications to Safely Repurpose Existing Pipelines to Transport Pure Hydrogen and Hydrogen-Blends" DOT/PHMSA Contract Number: 693JK322RA001

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by

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List of Acronyms

API	American Petroleum Institute
ASME	American Society of Mechanical Engineers
ASTM	American Society for Testing and Materials
CDM	Continuum Damage Mechanics
CE	Carbon Equivalent
C(T)	Compact Tension specimen
CVN	Charpy V-Notch
DOE	Department of Energy
DOT	Department of Transportation
ECA	Engineering Critical Assessment
EPRG	European Pipeline Research Group
FCGR	Fatigue Crack Growth Rate
Fe	Iron
GTN	Gurson-Tvergaard-Needleman
HE	Hydrogen Embrittlement
HEDE	Hydrogen Enhanced Decohesion
HELP	Hydrogen Enhanced Localized Plasticity
ILI	In-Line-Inspection
IMP	Integrity Management Plan
MnS	Manganese Sulfide
NG	Natural Gas
PEEQ	Equivalent Plastic Strain
PFM	Phase Field Modelling
PHMSA	Pipeline and Hazardous Materials Safety Administration
QC	Quasi-Cleavage
SNL	Sandia National Laboratories

Scope

There is considerable interest in evaluating existing natural gas (NG) pipelines for transmission of hydrogen. Use of existing pipeline infrastructure to transport NG blended with hydrogen is expected to play an integral role in the expansion of alternative fuels as part of efforts to reduce greenhouse gas emissions. In June 2023, the U.S. Department of Energy (DOE) published the *U.S. National Clean Hydrogen Strategy and Roadmap* [1], calling for net-zero greenhouse gas emissions by 2050. Similar initiatives are underway in Europe and Australia [2], [3]. The use of hydrogen will play an important role in reaching this objective. To make progress towards this goal, it is recognized that utilization of existing transmission pipelines and distribution networks will be necessary [4]. Existing pipeline networks are

mainly comprised of older line pipe put into service prior to about 1980. These "vintage" pipelines are generally regarded as having lower fracture toughness and a greater amount of fabrication flaws due to the steel manufacturing and fabrication practices in place during this time [5] compared to recently constructed pipelines. Moreover, existing vintage pipelines have been subject to damage over time that may represent an integrity threat when exposed to a hydrogen rich environment. It is important that the suitability of these lines to transport hydrogen is carefully considered. This will require knowledge of materials properties changes in this new environment, as well as engineering analysis procedures that account for the effects of hydrogen. This literature survey is focused on the implications of repurposing existing pipelines to hydrogen on various forms of damage. This is a complementary report to a prior literature survey addressing the review of threat integrity resulting from the introduction of hydrogen to vintage pipelines [6]. A particular focus will be on modeling approaches that have been applied to examine the mass transfer of hydrogen near defect locations, and the subsequent effects on integrity.

Introduction

There are many factors that must be considered when evaluating the potential for repurposing existing pipelines for hydrogen service. A primary issue is the defect tolerance of vintage pipelines containing various forms of damage. It is well established that hydrogen embrittlement (HE) reduces the fracture toughness, lowers tensile ductility, and increases the fatigue crack growth rate of steels [6][,] [7][,] [8]. However, the yield and tensile strength are only slightly influenced by the presence of hydrogen for ambient below-ground operation. While the effects of hydrogen on modern pipeline steels (defined here as post-1980) have been studied extensively, only a few efforts have focused on vintage steels [9], [10]. Vintage pipelines were typically constructed from lower-strength steels and have greater variability in properties due to antiquated steel manufacturing processes, comparatively poor chemistry controls, and varied fabrication methods [11]. Pipe mills were known to use a wide variety of heat treatment protocols leading to different weld microstructures and hence different sensitivity to hydrogen. High carbon equivalent (CE) coupled with rapid cooling, often inadvertently following welding, led to hard spots either in the pipe body or in the weld seams. These hard spots generally consisted of untempered martensite known to have poor toughness and greater susceptibility to HE compared with pearlitic microstructure. These locations have caused failures due to hydrogen charging from cathodic protection, where coating degradation has taken place and wet soil conditions exist [12].

One of the challenges in evaluating the effects of hydrogen on existing pipelines is the difficulty in determining the amount of hydrogen that enters steel. The processes by which molecular hydrogen dissociates, adsorbs on the steel surface, and is subsequently absorbed is highly complex. This makes experimental data extremely important in evaluating properties. This is further complicated by the effects of the stress-strain field around defects, which can result in local hydrogen concentration that is substantially greater than the bulk hydrogen content. This leads to a comparatively lower defect tolerance because of HE. By necessity, experimental data on material properties in hydrogen charged steels is important, preferably in a gaseous environment. While small scale lab tests can replicate the intended gas composition and loading conditions, there are still limitations regarding the degree of similitude that can be achieved [6]. To date, there is limited data on full scale pipe experiments looking at various forms of damage. This is a significant gap in validating small scale testing and predicting the effects of hydrogen on real defects. In Europe, a test program is being conducted in 2023 by the

European Pipeline Research Group (EPRG). This program will comprise of two materials, a modern X70 pipe and a 1970 vintage X60 pipe. The goal of the tests are as follows [13]:

- 1. Evaluate the effects of high hardness on material performance,
- 2. Compare material performance between manual and automated welding techniques of girth welds,
- 3. Compare fatigue crack growth rate (FCGR) results from small-scale tests to full-scale pipe tests, and
- 4. Estimate the fracture behavior of the seam weld after fatigue loading to the point of where the crack grows through the wall thickness.

It is hoped that the results of the full-scale tests can be correlated with the small-scale fracture and fatigue crack growth tests. Another active effort is being led by Sandia National Laboratories (SNL) called *HyBlend* https://www.energy.gov/eere/fuelcells/hyblend-opportunities-hydrogen-blending-natural-gas-pipelines. This is a government-private sector program looking at fatigue and fracture of line-pipe steels in hydrogen. It comprises four national laboratories, twenty-six industry/academia partners as well international partners. There are three main components to this project including material testing, probabilistic analysis, and physics-based mechanistic study. The testing program includes new as well as vintage steels – in particular X52 samples from the 1950's and 1960's. Data from this program suggests that impacts of hydrogen on properties such as fracture toughness are more pronounced for newer higher-toughness steels [14]. That is, for new high-toughness steels the drop in fracture toughness is much greater than for an older, lower toughness steel. Between these and other experimental programs currently ongoing, it is expected that in the coming years data will be available characterizing the behavior of vintage steels and welds in hydrogen.

Another area of active research deals with the modeling of HE effects on various forms of pipeline damage. Efforts are ongoing looking at topics such as hydrogen entry into steels, the effects of stress and strain on hydrogen diffusion, and modeling damage evolution. Current research at the University of Akron, Imperial College London, and Ghent University (amongst others), are developing finite element methods to predict the behavior of steels charged with hydrogen. These models describe the diffusion of hydrogen to regions of high stress-strain associated with pipeline damage, and then attempt to predict their behavior under load. These models are guided by results of mechanical tests for calibration of parameters. Most build on fairly mature continuum damage models (e.g., Gurson) [15], [16], [17], [18], [19], [20]. The application of these approaches can be valuable in gaining insight into changes in defect tolerance after the introduction of hydrogen.

Transmission pipelines are subject to various forms of damage, some introduced from original fabrication, and others occur over time. They can loosely be grouped into two categories; crack-like defects such as hook cracks or lack of fusion, or strain-based damage in the form of dents, wrinkle bends, or large displacements caused by external forces. The distinction becomes important when considering the best approaches for conducting an engineering critical assessment (ECA). Common integrity threats affecting pipelines include:

- Dents,
- Gouges,
- Wrinkle bends,

- Local corrosion thinning,
- Cracks from fabrication in welds (axial seam, girth, and in-service fabrication welds such as hot taps or repair sleeves),
- Fatigue/fatigue crack growth,
- Stress-corrosion crack growth,
- Hard spots (body or seam weld), and
- Strain soil water movement.

At the current time, the qualification of pipelines for hydrogen service follows the procedures in ASME B31.12 [21]. This standard addresses the design of new pipe and pipelines for hydrogen service. This engineering code has also been used as a basis to evaluate the suitability of existing pipelines, as no post-construction code currently exists addressing this topic. ASME B31.12 offers two options for materials selection. Option A is prescriptive in nature and provides design factors based on location class and restricts the maximum pressure for carbon steel to 3,000 psig. Option B is a performance-based standard that permits the use of less restrictive design factors but requires additional materials testing like those in Article KD-10 of ASME BPVC, Section III, Division 3

At this time, it has been proposed that the B31.12 standard may become significantly revised so that pipeline aspects would be included in B31.8 and piping would be in B31.3.

This report will focus on recent developments for evaluating the effects of hydrogen on pipeline damage. A critical component in repurposing pipelines for hydrogen service will be development of an appropriate inspection and assessment protocol, and development of an integrity management plan (IMP) that addresses the change in threat posed by transport of hydrogen. A general summary of the effects of hydrogen on mechanical properties of pipeline steels was provided in a companion report [6].

Before proceeding with this report, it is important to discuss the thermodynamics aspects of hydrogen transport in steel considering the influence of stress and strain, as these are fundamental topics related to the study of HE.

Thermodynamics of Hydrogen in Steels

A key element in understanding the effects of HE starts with the process by which molecular hydrogen dissociates and enters steel. As mentioned previously, this is a highly complex topic, and a detailed mechanistic description is outside the scope of this report. However, some discussion is important to gain insight into how the introduction of hydrogen in pipelines might affect mechanical integrity. Hydrogen can enter steel through various means, but of most importance to pipelines includes corrosion reactions in sour environments, electrolytically by cathodic charging, or by exposure to a hydrogen rich gaseous environment. Most of the studies looking at hydrogen ingress have focused on cathodic charging where the experimental and theoretical understanding is well developed. The uptake of hydrogen permeation in a gas environment takes place by a completely different mechanism than cathodic charging. The process involves first dissociation of molecular hydrogen, then adsorption on the metal surface, i.e., the hydrogen atoms stick to the surface of the pipe. At equilibrium, a linear concentration profile develops as the flux into and out of the steel remains constant. This is illustrated in Figure 1.



Figure 1 Illustration of hydrogen dissociation and adsorption, from Sun et al. [22]

Hydrogen has been found to enter Fe on preferential crystallographic planes in which there is favorable thermodynamic driving force. This process is extremely difficult to study experimentally, though some advanced analytical techniques have been used to establish the adsorption structure of hydrogen on Fe. Sun et al., have studied this using modelling techniques to explore the thermodynamics of this process to explain questions about the entry of hydrogen into steels at different temperatures and pressures, and potential effects of other gasses such as methane [22]. Their calculations show, for example, that methane does not participate in the dissociation or adsorption of hydrogen, only acting as a diluent affecting the partial pressure hydrogen. With increasing hydrogen partial pressure and higher temperature, the thermodynamic driving force for hydrogen entry into iron (or steel) also increases. At ambient temperature and pressures in the range of pipeline operation, there are other factors that influence the efficiency of hydrogen entry. Preferential trapping sites such as grain boundaries or dislocations, or tensile stress all facilitate hydrogen uptake. An important factor that will influence the dissociation and adsorption of hydrogen is the presence of surface oxides or corrosion scale, which will tend to interfere with the dissociative adsorption process. However, the protective nature of surface scale is unlikely to remain over long times, and it should be assumed that hydrogen ingress will take place as demonstrated by the theoretical calculations of Sun et al., [22]. In the work by Groeneveld et at., they also showed that shot blasting of the surface of the soft base metal can also reduce the hydrogen flux through the steel [23].

Hydrogen Solubility and Diffusivity

The concentration of hydrogen in steel is a function of the trapped hydrogen and the lattice concentration $C_{total} = C_T + C_L$. The source of the trapped hydrogen comes from many sources including grain boundaries, dislocations, vacancies, as well as various inclusions such as carbides or sulfides. Manganese sulfide (MnS) is of relevance to vintage pipelines as they generally contain higher amounts of sulfur. Hydrogen trapping associated with these inclusions are classified as dynamic sinks. Accumulation at MnS inclusions will continue as hydrogen uptake proceeds. This is caused by void formation at the interface between the inclusion and the steel matrix where hydrogen recombines into molecular form. This is often observed as blistering in steels charged with hydrogen in aqueous solution containing H₂S. Another factor that affects hydrogen concentration on a local scale is the presence of high hydrostatic (tensile) stress given as $\sigma_H = \left(\frac{\sigma_1 + \sigma_2 + \sigma_3}{3}\right)$. At these locations, the Fe crystal lattice dilates and can accommodate a greater number of hydrogen atoms. Conversely, compressive hydrostatic stress has the opposite effect. Plastic deformation also increases solubility due to higher dislocation density. An example of this is at the tip of a crack, where the local stress-strain field attracts and concentrates hydrogen. This is illustrated in Figure 2.



Figure 2 Schematic illustrating hydrogen concentration at crack tip

The plot shows the normalized stress field ahead of the crack in a compact tension C(T) specimen along with the equivalent plastic strain (PEEQ) versus distance, normalized by the yield stress and J integral. As will be discussed later, the region of high stress-strain near the crack tip, referred to as the fracture process zone, coincides with the location of highest hydrogen concentration.

San Marchi and Somerday have summarized the thermodynamics of gaseous hydrogen to explain the solubility and transport characteristics [24]. At equilibrium, the chemical potential of molecular hydrogen, μ_{H_2} , in the gas and the atomic hydrogen dissolved in the Fe crystal lattice are equal.

$$\frac{1}{2}\mu_{H_2} = \mu_L \tag{1}$$

The chemical potential can be written as [24]:

$$\frac{1}{2} \left[\mu_{H_2}^o + RT ln\left(\frac{f_{H_2}}{f_{H_2}^o}\right) \right] = \mu_H^o + RT ln(a_H)$$
(2)

Where f_{H_2} is the fugacity of molecular hydrogen, $f_{H_2}^o$ is hydrogen fugacity at the standard state, R is the gas constant, T is temperature (°K), and a_H is the activity of hydrogen dissolved in the Fe lattice. Note that at typical pipeline operating pressures the hydrogen fugacity is \approx partial pressure. Since the concentration of dissolved hydrogen is very low, the activity, a_H , is equal to the concentration of hydrogen in the Fe lattice c_L . It is observed by San Marchi et al., that Equation (2) is the basis of *Sievert's*

^{*} The chemical potential, μ_i represents the change in Gibbs free energy at constant temperature and pressure, when atoms are added or removed from the system; $\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_i}$.

Law, which states that the solubility of a diatomic gas in metals is proportional to the square of its partial pressure [24]:

$$K = \frac{C_L}{\sqrt{f}}$$
(3)

Where K is the equilibrium coefficient given by,

$$K = K_o(T)exp\left(-\frac{\Delta H_s}{RT}\right)$$
(4)

In Equation (4), ΔH_s is the enthalpy of the solution. Drexler et al. have derived a generalized form of Sievert's law including the effect of trapping sites and stress [25]. Their equation is given as:

$$C_H = K_o(T)\sqrt{f} \exp\left(-\frac{\Delta H_s - \sigma_H V_H}{RT}\right)$$
(5)

The term $K_o(T)$ accounts for the temperature-dependent solubility coefficient $K_o \cong K'_o \cdot g(N_L, N_T, K_T)$. Here K_T is given by,

$$K_T = exp\left(\frac{-E_b}{RT}\right) \tag{6}$$

Where E_b is the binding energy. Drexler approximates $K_o(T)$ as,

$$K_o(T) \cong K'_o \cdot N \cdot \left(1 + \frac{N_T}{(N \cdot K_T)}\right) / N_L$$
⁽⁷⁾

Here N_L is the density of interstitial lattice sites, N_T is the density of trap sites, $N = N_L + N_T$, and K'_o is a constant. Values for the various parameters from Drexler et al. are given in Table 1.

Parameter	Symbol	Value	Units
Binding Energy	E_b	30	kJ/mol
Constant pre-factor	K'_o	33	wppm/Vbar
Density interstitial lattice sites	N_L	8.5x10 ⁻⁴	mol/mm ³
Partial molar volume	V_H	2000	mm³/mol
Solution enthalpy	ΔH_s	27	kJ/mol
Density of trap sites	N_T	1x10 ⁻⁷	mol/mm ³
Hydrostatic stress	σ_{H}	-	MPa
Fugacity	f	-	bar

Table 1Parameters used to estimate hydrogen concentration [25]

Using Equation (5), the hydrogen concentration at ambient temperature (25°C) as a function of hydrogen pressure, including the effect of hydrostatic stress σ_H , is shown in Figure 3.



Figure 3 Effect of hydrostatic stress in hydrogen solubility following Drexler et al., [25]

In this example, the hydrogen pressure varies from 0 to 200 MPa for a thin-walled pipeline with a diameter of 800 mm, and wall thickness of 10 mm. The hydrostatic stress is given by the trace of the stress tensor:

$$\sigma_H = \frac{1}{3} tr(\boldsymbol{\sigma}) \tag{8}$$

At 200 bar, the increase in hydrogen solubility is about 18% greater when the solubility is estimated with addition of the hydrostatic-stress term. The dashed line in Figure 3 represents the hydrogen concentration as estimated by Sievert's Law.

As alluded to earlier, plastic strain also influences hydrogen solubility. This is attributed to the increased dislocation density caused by the permanent deformation of the Fe crystal lattice resulting from an applied shear stress. This is illustrated pictorially in Figure 4.



Figure 4 Illustration of dislocation accommodating hydrogen atoms

Here the Fe lattice is distorted due to the shear stress creating a dislocation that can accommodate hydrogen. Results of numerical analyses have been conducted evaluating the hydrogen distribution at the tip of a blunting crack, taking account of local plasticity effects [26], [27], [28]. The empirical relationship developed between trap sites N_T and plastic (equivalent) strain ε^p is given as follows.

$$\log(N_T) = 23.26 - 2.33 exp(-5.5\varepsilon^p)$$
(9)

Shown in Figure 5 is a plot of Equation (9) Illustrating that the density of trap sites saturates at a strain fraction of about 0.8.



Figure 5 Increase in trapping sites N_T with plastic strain ϵ^p [28]

Note that an increase in strain fraction from zero to 0.2 results in a change in trap density from 10^{21} to $10^{22.5}$ trap sites per cubic meter.

Hydrogen Trapping

As mentioned earlier, solubility and diffusivity are affected by the trapping of hydrogen at various sites such as defects in the Fe crystal lattice, dislocations, grain boundaries, void formed by interfaces at nonmetallic inclusions, etc. These trap sites can be described as reversible and irreversible, based on the energy required to release hydrogen, i.e., the binding energy E_b , illustrated in Figure 6. Hydrogen diffusion is governed by the rate at which atoms hop between interstitial lattice sites, and the extent of atoms temporarily trapped. There are numerous sources of hydrogen traps; however, hydrogen transport is generally governed by only one or two types. Sites that have sufficiently low binding energy that hydrogen may be released are referred to as reversible traps, and those in which the binding energy is high are referred to as irreversible traps [29].



Figure 6 Schematic illustrating effect of reversible and irreversible trap sites on diffusivity [30]

Definitions for Figure 6 are as follows;

Normal interstitial site,
Reversible trap site,
Activation energy for lattice diffusion,
Activation energy for de-trapping (reversible trap),
Reversible trap binding energy,
Irreversible trap binding energy, and
Saddle point energy.

There is not a strict cutoff defining the reversibility of trap sites. Reversibility is a probabilistic matter governed by the distribution of binding energies of various trap sites and thermal energy supplied. Plastic strain affects the apparent diffusivity by increasing the number of trap sites. The apparent diffusivity is described by the following relation.

$$D_{app} = \frac{D_L}{1 + \lambda_T} \tag{10}$$

Where λ_T is the trapping-capacity factor defined $\lambda_T \equiv \frac{K_T N_T}{N_L}$. Huang et al. [31], studied the effect of strain-induced traps on apparent diffusivity for iron. Figure 7 shows a plot of their results of diffusivity versus static prestrain (and associated stress to attain the prestrain). Note that elastic strain does not affect diffusivity.



Figure 7 Effect of prestrain on apparent diffusivity, D_{app} [31]

At a prestrain of 0.14, the apparent diffusivity has decreased from about 25 x 10^{-6} cm²/s to 2 x 10^{-6} cm²/s, or one order of magnitude. They also estimated the surface concentration, C_o , versus prestrain, shown in Figure 8.



Figure 8 Effect of prestrain on hydrogen surface concentration, C_o[31]

Here, there is almost one order of magnitude increase in C_o with a prestrain of 0.14. This has important implications for the evaluation of damaged regions of a pipeline. In high strain locations like dents or wrinkle bends, for example, the hydrogen distribution will concentrate in regions of high strain (damage).

Practical Example: Shot Peening of Steels

A study performed by Wang et al., looked at the effect of shot peening on the hydrogen transport in steel [32]. This work is particularly useful in gaining insight into the way stress and strain affect hydrogen distribution. Their research looked at the effect of shot peening on the near surface stress and strain fields and their impact on the transport of hydrogen. They explained the apparently anomalous

observation that in a mildly hydrogen charging environment, shot peening appears to have a beneficial effect in minimizing HE. However, in a severe hydrogen charging environment, shot peening seems to enhance the degree of hydrogen absorption. Here severity of the environment refers to either the hydrogen fugacity (pressure) in the gas phase, or hydrogen activity in solution. Finite element simulations of shot peening were conducted to estimate the magnitude of stress-strain fields as a function of various parameters such as shot velocity. Provided in Figure 9 are results showing a high compressive hydrostatic stress near the surface to a depth of about 0.2 mm. The corresponding equivalent plastic strain reached 20% at a depth of 0.1 mm, and decays to zero at 0.2 mm. Wang et al., first solved for the hydrogen distribution using a classical diffusion analysis through Fick's Law. Next, they included the effects of hydrostatic stress (in an analogous fashion Drexler et al. [25]) and plastic strain. The influence of strain on solubility is accounted for by using an empirical relationship very similar to Equation (9). Including the effect of plastic strain (hydrogen trapping) on apparent diffusivity D_{app} , they use the following expression from Oriani [33]:

$$D_{app} = \left(\frac{C_L}{C_L + C_T (1 - \theta_T)}\right) D_L \tag{11}$$

Here D_L is the lattice diffusivity ignoring any trap effects, and θ_T is the occupancy of trap sites where $\theta_T = \alpha \frac{C_T}{N_T}$, and α is denotes the number of sites per trap, taken as 1, which is a function of the local effective plastic strain.

There is a somewhat complicated interplay between diffusion as described by Fick's Law, the state of stress, and the presence of plastic deformation (strain). Shot peening induces a compressive stress near the surface, as shown in Figure 9 (a). This has the effect of *decreasing* the hydrogen solubility on this region. The resulting strain field shown in Figure 9 (b), is expected to *increase* solubility by the creation of trapping sites for hydrogen as shown in Figure 5.





However, the increased solubility (and trapping) of hydrogen has the effect of slowing the effective diffusion rate (D_{eff}).

Numerical simulations were undertaken by Wang et al., looking at the effects of shot peening on hydrogen distribution for the cases of diffusion only, diffusion plus stress, and combined effects of diffusion, stress, and plastic strain [32]. Their simulation for a low severity case, where the initial surface concentration was $C_{L,0} = 15 \frac{mol}{m^3}$, and shot velocity is 50 m/s is shown in Figure 10⁺. This shows that the presence of compressive stress decreases the surface concentration significantly compared with the diffusion-only case. However, the combined effect including plastic strain results on an overall decrease in the hydrogen concentration throughout the thickness. While the region of high plastic strain near the surface will accommodate more hydrogen, the net effect is to lower the overall concentration profile due to the decrease in diffusivity.



Figure 10 Normalized hydrogen concentration profile for low-severity environment [32]

The same analysis was also performed for a "severe" hydrogen environment where $C_{L,0} = 60 \frac{mol}{m^3}$ with shot velocity still 50 m/s. In this case, the hydrogen concentration profile and the transport rate are less affected by plastic deformation shown in Figure 11.

⁺ Note $1\frac{mol}{m^3} = 0.13 \text{ wt ppm}.$



Figure 11 Normalized hydrogen concentration profile for high severity environment [32]

Here the high surface concentration of hydrogen is less affected by plastic deformation, but the compressive stress still reduces the concentration to the depth of 0.2 mm, after which it is like the diffusion-only case (see Figure 10).

The effect of plasticity on hydrogen concentration is also demonstrated by experiments in which specimens are subject to tensile pre-strain prior to testing. Shown in Figure 12 are results from Dutkiewicz et al., on the effects of pre-strain on notch ductility [34].



Figure 12 Effect of plastic deformation on hydrogen concentration [34]

In Figure 12 (a), the hydrogen concentration is shown as a function of pre-strain. In line with the previous discussion, the hydrogen concentration increases with plastic strain. In Figure 12 (b), the corresponding stress-strain curves show an associated reduction in fracture strain.

This discussion highlights the complex nature of the competing forces that influence hydrogen solubility and transport in metals.

Key Take-Aways

- 1. Hydrogen solubility is governed by Sievert's Law, $K = \frac{C_L}{\sqrt{f'}}$
- 2. Tensile (hydrostatic) stress increases solubility, while compressive stress decreases solubility,
- 3. Plastic strain increases solubility by increasing dislocation density, and decreases diffusivity
- 4. Gradients in concentration, stress, and plastic strain all affect the resulting hydrogen distribution.

To this point, only thermodynamic considerations have been described. For real cases, either in the lab or in the field, surface effects will influence the permeability of hydrogen through steels. As a practical matter, it must be assumed that over time hydrogen will eventually diffuse into a pipeline steel. However, it is useful to discuss some of the relevant literature on this topic.

Effect of Surface Condition on Hydrogen Charging

As discussed previously, hydrogen enters steel through a process of dissociation and adsorption. The kinetics of adsorption are strongly affected by the surface condition. Barriers to hydrogen entry into steels can be classified as either physical barriers or gaseous inhibitors. Physical barriers are considered here to be either intentionally introduced by surface modification (e.g., vapor deposition) or naturally occurring due to the formation of iron oxides or corrosion scale. While the application of deposition coatings is not practical for transmission pipeline applications, the effect of surface oxides is relevant to the current discussion.

Hydrogen Permeability

Permeability is the rate of flux of hydrogen atoms passing through the material. This is described mathematically as the product of diffusivity and solubility.

$$P_m = D_o exp\left(-\frac{Q}{RT}\right) \cdot S_o exp\left(-\frac{\Delta H_s}{RT}\right)$$
(12)

The solubility and diffusivity of hydrogen in common iron oxides (Fe_2O_3 and Fe_3O_4) is substantially lower than for carbon steel (α -iron), effectively can be considered nil. The presence of an oxide scale also suppresses hydrogen uptake [35]⁷ [36]. In fact, experimental studies have shown that the presence of oxygen mitigates the effects of the deleterious decrease in the plastic part of the load-displacement curve in a fracture test, as illustrated in Figure 13 [37]. This shows the increase in load-displacement curve (higher fracture toughness) with the addition of small amount of oxygen. The beneficial effect of oxygen may be attributed, to a large extent, to the presence of surface oxides.



Figure 13 Effect of oxygen on plastic part of load-displacement curve in a fracture test [37]

Internal pipeline corrosion for NG transmission lines is due to a variety of sources related to contaminants in the product stream. The primary constituent of rust is Fe_2O_3 (hematite). Work by Xing et al. [38] has looked at the presence of Fe_2O_3 as a diffusion barrier to hydrogen. They performed detailed molecular dynamics calculations looking at the energetics associated with adsorption and diffusion in pure Fe and Fe_2O_3 . These types of physics-based calculations enable the study of surface effects like the process of hydrogen entry into steel (Fe) that are extremely difficult to study experimentally. They are proving to be increasingly valuable in the study of hydrogen compatibility of steels. Xing et al., found the adsorption energy on the Fe_2O_3 surface was much smaller than hydrogen on the Fe surface. This indicates that Fe_2O_3 can reduce the amount of hydrogen atoms available to enter the Fe crystallographic structure, acting as a barrier to hydrogen adsorption. The analysis also indicated that hydrogen diffusivity in Fe_2O_3 is essentially nil at temperatures below $620^\circ F$ ($600^\circ K$). This is illustrated in Figure 14.



Figure 14 Estimated diffusivity of hydrogen in Fe and Fe₂O₃ [38]

This analysis shows that if a tenacious, defect free oxide scale (rust) is present on steel pipelines, it would represent an effective barrier to hydrogen entry. In reality, though, surface oxides and corrosion scale present on the internal surface of NG transmission pipelines cannot be relied upon to provide long-term barrier to hydrogen ingress.

Hydrogen Embrittlement of Steels

Many different mechanisms have been proposed to explain "hydrogen embrittlement" of steels. These models attempt to provide a fundamental understanding of the mechanical behavior of hydrogen charged steels, as well as the fracture mechanisms observed. These models strive to explain observations such as ductile-to-brittle transition, strain-rate effects, loss in notch ductility, reduction in fracture toughness on the upper-shelf, etc. They also must address behavior on the microscopic scale such as the fracture mode, which can be brittle intergranular/transgranular (quasi) cleavage, or ductile microvoid coalescence. The operative mechanisms can change based on factors such as microstructure, loading, and hydrogen-charging conditions. Robertson et al., provide an excellent summary of the development of HE research and the mechanistic understanding [8]. Two models that have emerged providing the most viable theories include hydrogen-enhanced decohesion (HEDE) and hydrogen-enhanced localized plasticity (HELP).

Hydrogen-Enhanced Decohesion (HEDE)

The underlying principle behind the decohesion model is that the presence of hydrogen in the Fe crystal lattice reduces the bond strength, leading to fracture at a lower stress transverse to the crystallographic planes. It can also be viewed as lowering the surface energy promoting fracture along cleavage planes or along grain boundaries. In either case, the accumulation of hydrogen at a crack tip reduces the stress required for fracture. As illustrated in Figure 2, hydrogen will migrate to the fracture process zone just ahead of a crack due to the high stress-strain gradients. The concept that hydrogen dissolved in the crystal lattice reduces surface energy is well aligned with the Griffith theory of fracture. Both use a thermodynamic basis, where the energy stored in the structure must overcome the surface energy of the material. The Griffith criterion gives the fracture stress as [39] ;

$$\sigma_f = \left(\frac{2E\gamma_s(H)}{\pi a}\right)$$

Where $\gamma_s(H)$ is the surface energy when hydrogen is present, E is the total energy, and a is the crack size. This topic will be revisited in the context of phase-field modeling approach to fracture in a later section.

Hydrogen-Enhanced Localized Plasticity (HELP)

The HELP mechanism stems from the observation that under various loading conditions, the presence of hydrogen enhances dislocation motion [40]. One of the first to study this was Beachem, who found that low-pressure hydrogen induced microvoid coalescence [41]. Later studies by a research group at the University of Illinois led by Birnbaum, Robertson, and Sofronis, using high-resolution microscopy, showed that the presence of hydrogen enhanced the motion (velocity) of dislocations, even under constant stress [42]. In these experiments, very small test specimens are loaded within the vacuum chamber of the electron microscope, and then hydrogen is introduced. Dislocation motion can then be observed directly under different conditions. This mechanism postulates that in the high-stress region just preceding a crack tip, where hydrogen will concentrate, *local* plastic strains are enhanced which impacts the fracture processes and in turn the resistance to fracture, which could be brittle in nature.

Fracture Modes in Hydrogen

From an engineering standpoint, the various models for HE assist in explaining the macroscopic properties and fracture modes of steels exposed to a hydrogen environment. In this section, the two most cited HE mechanisms just discussed will be related to the mode of fracture. There is still extensive research ongoing looking closely at these and other mechanisms as well as the role of hydrogen on available fracture pathways. The fracture mode is influenced by several factors including hydrogen content, microstructure, loading rate, etc. Considering first the HEDE mechanism, characterized by weakening of interatomic bonds, results in tensile separation of atoms in lieu of dislocation motion along slip planes. As discussed by Lynch [43], very high elastic stresses are required to produce decohesion in the lattice plane ahead if a crack tip. For transgranular cracking, decohesion can take place via several processes including at; (a) atomically sharp crack tip, (b) in the region just preceding the crack tip where dislocation shielding effects result in the maximum tensile stress, (c) at particle-matrix interfaces in the fracture process zone, or (d) the location of highest hydrostatic stress where the hydrogen concentration is likely to be highest. A fracture mode unique to HE is referred to as quasi-cleavage (QC). This is characterized by fracture along non-cleavage planes with ridges running in line with the crack growth direction. Shown in Figure 15 is an SEM image of a fracture surface exhibiting quasi-cleavage in an API X60 steel.



Figure 15 SEM images of quasi-cleavage of API X60 steel tested in hydrogen, from Martin et al. [44]

The striations or river markings shown in Figure 15(a) are caused by crack growth within individual grains. While the appearance is very similar to transgranular brittle cleavage observed in steels at low temperatures, fracture path is not following the cleavage planes associated with ferritic (body-centered cubic) material. Figure 15(b) is a higher magnification image revealing the striations are actually ridges, indicated by arrows, caused by the final *ductile* separation of the fracture surface. Nevertheless, while ductile processes govern behavior on a local or small length scale, macroscopically steels charged with hydrogen are characterized by fracture having limited deformation.

Grain boundaries are locations where the hydrogen concentration will be high and interatomic bonds are already weakened. This is illustrated in Figure 16. Therefore, intergranular fracture can represent a potential pathway for crack advance via a decohesion mechanism. The factors that drive the morphology of fracture are complex. Generally, though, lower stress fractures tend to exhibit intergranular morphology while higher stresses lead to intragranular failure. Often mixed modes are observed because of local stress state, presence of second phase particles such as MnS inclusions, and other factors.



Figure 16 Grain-boundary cohesive energy in hydrogen [42]

Shown in Figure 17 is an SEM image showing a mixture of intergranular fracture and QC in a martensitic steel.



Figure 17 (a) mostly intergranular fracture, and (b) mixed intergranular and quasi-cleavage(shown by arrows) [45]

Effects of Hydrogen on Mechanical Properties

In a prior review, data were presented on the effects of hydrogen on the mechanical properties of steel [6]. Therefore, only a short summary is repeated here for convenience. A good source of data for pipeline steels is available from Sandia National Laboratories[‡].

Tensile Properties

The influence of hydrogen on tensile properties is predominantly on failure strain. In most cases the yield and tensile strength are not significantly affected, though the tensile properties can influence the degree to which ductility is lost. That is, higher strength steels tend to suffer a greater loss in ductility compared with low strength steels. This is illustrated in Figure 18. Here the elongation at failure decreases with increasing hydrogen pressure. There is little change in the yield strength, and no discernable correlation between environment and ultimate tensile strength.

[‡] Sandia Hydrogen Effects Database



Figure 18 Effect of hydrogen pressure on failure strain at fixed strain rate [46]

Fracture and Fatigue Crack Growth rate

Both fracture toughness as well as fatigue crack growth resistance are degraded by hydrogen. A significant amount of data has been developed establishing this correlation, primarily for newer pipeline steels intended for new lines. While the literature is not as extensive for older vintage pipeline steels that represent most existing lines, the trends are consistent. Figure 19 shows data on FCGR for an X42 steel showing a significant increase in growth rate in hydrogen.



Figure 19 Effect of hydrogen on fatigue crack growth, from San Marchi et al. [47]

There is also a decrease in fracture toughness caused by hydrogen, as shown in Figure 20.



Figure 20 Reduction in fracture toughness for X42 steel tested in hydrogen [47]

Subcritical Crack Growth

An important question regarding the introduction of hydrogen into existing pipelines is the potential for subcritical crack growth – in this under constant load not cyclic load. The parameter of interest is K_{IH} , which represents the minimum stress intensity required to cause stable crack growth determined by a slow-rising displacement test. As shown in Figure 21, the value of K_{IH} is sensitive to loading rate due to the kinetics associated hydrogen diffusion to the crack tip. This trend might be important when looking at critical crack sizes since the burst pressure under sustained loading may be lower than the traditional burst test of slowly increasing the pressure to failure.



Figure 21 Stress intensity required for stable crack growth, K_{IH} under constant load [48]

Full-Scale Testing

Due to the difficulty in performing full-scale burst testing with hydrogen, very little test data is available, although programs are currently underway in Europe and likely elsewhere. One of the few data sets was developed by Sandia National Laboratories in 1978-79 [49]. Interestingly, the motivation for the work was the repurposing of NG pipelines to carry hydrogen. The tests were carried out on A106 Grade B pipe of 4" diameter, with an internally machined axial flaw 20% through the wall thickness. The tests were conducted at 50°F. Results from this program are shown in Figure 22. The data indicates a reduction of approximately 15-20% in burst pressure due to hydrogen. The reader is cautioned that full details of the experimental procedures are not available publicly, and the data are shown only to indicate the general trend observed in this study. Such trends, of course, change with different materials, pipe sizes, and crack sizes; so, 20% is not a general value that should be employed.



Figure 22 Burst test data for axially flawed pipe in nitrogen and 1,000 psi hydrogen [49]

Damage Modelling

The suitability of existing pipelines for hydrogen service is an important question currently being considered as part of the drive to rapidly expand the use of emerging fuels. This is both an economic question and a critical safety concern. The two are closely related by determination of acceptable service conditions meeting safety expectations that may or may not result in favorable economics for repurposing a pipeline to hydrogen. Moreover, each pipeline has a unique service and manufacturing history that will likely influence the safe operating limits. It is therefore important that tools exist for evaluating lines and development of appropriate operating envelopes for hydrogen service. This will involve several factors, but chiefly the development of material property data, capabilities of in-line-inspection (ILI), and development of new engineering analysis methods suitable for evaluating various forms of damage in the presence of hydrogen. New analysis methods are rapidly emerging aimed at evaluating the effect of damage on integrity taking account of the changes in properties in the new service conditions. These techniques involve advanced multi-physics methods that incorporate damage algorithms informed from phenomenological models of HE – namely the HEDE and HELP mechanisms.

Test data are currently being developed at numerous laboratories around the world for calibration purposes. There also exists an extensive body of literature on the transport properties for hydrogen and steels that enable estimation of hydrogen content and distribution.

Modeling of this type offers the potential to compare damage in pipelines in current NG service with a hydrogen environment, enabling a comparison in the relative change in mechanical integrity when repurposing a pipeline. Due to the cost and time required to conduct full-scale testing, this approach provides a means of exploring integrity issues and operating limits for pipelines with various forms of damage. Test parameters can then be developed to tune and validate models.

Continuum Damage Mechanics (CDM)

Continuum damage mechanics involves modeling damage in a component subject to property degradation and an applied load. A state variable is defined that describes the damage evolution as a function of time and/or changing load. Damage is defined in terms of the properties affected, such as loss of ductility. CDM incorporates a material model informed by analysis of damage mechanisms on a small length scale. The models are tuned by material test results so that analyses can be made on the component level. This is illustrated in Figure 23, showing CDM in terms of length scale.



Length Scale

Figure 23 Illustration of CDM on length scale

To characterize HE, information on the atomistic and microscopic length scales are used to develop models for the concentration and diffusion of hydrogen near cracks or other defects. Phenomenological models are then used to describe material properties and the effect of hydrogen on defect behavior. These inputs are then used in a finite element model that discretizes the geometry of a component to analyze damage evolution, and ultimately predict the loss of structural integrity.

In the area of HE research, work is ongoing in the U.S. as well as Europe developing CDM approaches to predict the integrity of pipelines after conversion from NG to hydrogen. There are a number of approaches that have been taken, but two have received the most attention recently. The first involves the use of a micromechanical damage model based on the nucleation and growth of voids to simulate ductile fracture. This method was developed by Gurson, Tvergaard and Needleman, and is therefore

referred to as the GTN model, [50][•] [51]. This approach has been widely used to evaluate the structural integrity of components including pipelines, particularly with respect to simulating burst testing of cracked or dented lines. Since the modeling of HE involves both the mass diffusion of hydrogen as well as mechanical loading, these mechanisms may be executed in a coupled or non-coupled manner. That is, the hydrogen diffusion problem may be solved first, and then the loading condition applied to analyze the structural behavior. The uncoupled approach has the drawback that the interaction between hydrogen diffusion and stress is not fully captured. Coupled models are more complex and computationally intensive but provide more accurate results as they solve the diffusion and stress-strain equations simultaneously. The second approach is referred to as phase field analysis. This is a very powerful approach in modeling fracture processes that can vary from brittle to ductile in nature. These methods will be described further, and some results presented, including preliminary work conducted as part of this project.

Gurson-Tvergaard-Needleman (GTN) Descriptions of Hydrogen Damage in Pipelines

GTN analysis is widely used to simulate ductile failure following void nucleation, growth, and coalescence. The basic principle is that as a material deforms under load, voids eventually form as strain accumulates and reaches some critical value. As the voids grow and coalesce, there is a reduction of load bearing capacity or stiffness of the structure. The GTN formulation defines a yield function $\phi(\sigma, \overline{\sigma}, f)$ that incorporates variables describing void nucleation and growth. The typical form of the GTN model is given by the following.

$$\emptyset(\boldsymbol{\sigma}, \bar{\sigma}, f) = \left(\frac{\sigma_e}{\bar{\sigma}}\right) + 2q_1 f \cdot \cosh\left(\frac{q_2 \sigma_m}{2\bar{\sigma}}\right) - 1 - q_3 f^2 = 0$$
(13)

Where σ is the stress tensor, f is the void volume fraction, σ_e is the equivalent stress, σ_m is the mean stress $\sigma_m = \frac{\sigma_1 + \sigma_2 + \sigma_3}{3}$ and q_i are material fitting parameters. The fitting parameters are typically derived from matching model prediction of stress-strain curve to notched tensile test data[§]. When a load is applied, the value of f increases and the yield surface decreases. In this model, f represents the damage variable. The rate of void growth \dot{f} is a function of the strain rate $\dot{\varepsilon}_n$:

$$\dot{f} = (1 - f)\dot{\varepsilon}_p \tag{14}$$

Yu et al. were among the first to model HE assuming a HELP mechanism using this approach [52], they refer to as "HGurson". The GTN approach is a sensible choice for damage modeling as it is based on ductile failure; recall the HELP theory of HE assumes localized plasticity. Assuming J_2 flow theory (non-linear elastic behavior).

$$\sigma_f = \sigma_o(c) \left(1 + \frac{\varepsilon_p}{\varepsilon_o} \right)^n \tag{15}$$

Where σ_f is the flow stress, $\sigma_o(c)$ is the yield stress as a function of hydrogen concentration (c), ε_p is the plastic strain, and ε_o is the yield strain $\varepsilon_o = \frac{\sigma_o}{E}$. To model the HELP mechanism, the flow stress is

[§] Notched bars are typically used to capture stress triaxiality effects.

reduced as a function of hydrogen concentration. This is implemented by reducing the yield stress as a function of increasing hydrogen concentration in a linear manner.

$$\sigma_{o}(c) = \begin{cases} \left[(\omega - 1) \frac{c}{c_{L}^{0}} \right] \sigma_{o} \text{ for } \sigma_{o}(c) > \gamma \sigma_{o} \\ & \text{or} \\ \omega \sigma_{o} \text{ for } \sigma_{o}(c) \le \gamma \sigma_{o} \end{cases}$$
(16)

Where σ_o is the initial yield stress without hydrogen, ω is effectively a softening parameter, c_L^0 is the initial hydrogen lattice concentration, and $\gamma \sigma_o$ is the initial yield stress at the starting hydrogen concentration, i.e., determines the lower-bound initial flow stress. Hydrogen trapping and diffusivity are accounted for in the manner described in the prior section covering diffusion and solubility. To include the effects of constraint, the fracture strain is made to be a function of stress triaxiality and hydrogen concentration, $\varepsilon_f(\frac{\sigma_h}{\sigma_o}, c)$. Results from Yu et al., are shown in Figure 24.



Figure 24 GTN analysis of notched bar from Yu et al. [52]

As expected, the normalized hydrogen concentration in Figure 24(a) is greatest in line with the location of highest hydrostatic stress. Similarly, the yield stress Figure 24(b) is lowest following the hydrogen concentration. The predicted stress-strain curve derived from the analysis is shown in Figure 25.



Figure 25 Stress-strain curve predicted from GTN analysis of HE notched tensile bar from Yu et al. [52]

Once the stress-strain prediction is calibrated with test data, it is possible to model the behavior of engineering structures charged with hydrogen such as pipelines.

Recent work published by Depraetere et al., employed a fully coupled GTN model to explore HE [16]. They evaluated the crack tip stress-strain field and associated initial hydrogen concentration. This was done using a 2D modified boundary layer model following the general approach of Sofronis and McMeeking [27], in which the crack-tip region is subject to plane-strain conditions to which a uniform displacement field is applied resulting in a target stress intensity. This is illustrated schematically in Figure 26^{**}.



Figure 26 MBL model of a crack with uniform initial hydrogen concentration, from Depraetere [16]

The distribution of hydrogen around the crack tip was simulated over time due to the evolving stressstrain field. The results are shown in Figure 27.

^{**} Background on the MBL approach to evaluating crack-tip stress-strain fields is found in Reference [64].



Figure 27 Simulation of hydrogen concentration around a crack tip in the MBL model [16]

In Figure 27, the normalized hydrogen concentration is plotted versus a normalized distance from the crack tip. One can envision that as the hydrogen concentrates around the crack tip, the flow stress is decreased and resistance to crack growth is diminished. This represents the current understanding of stable crack growth of a crack in a hydrogen charged material subject to a critical stress intensity, in line with the HELP mechanism.

Phase-Field Approach

Application of phase-field modelling (PFM) to fracture problems has gained in popularity over the last decade or so based on its ability to handle problems not well suited to more traditional approaches. PFM overcomes the limitations of discontinuity-based methods addressing crack nucleation, propagation, coalescence, and branching. This enables the behavior of fracture in real structures to be modeled in a more realistic manner. This is accomplished by introducing a damage variable that varies from $0 \rightarrow 1$, where a crack is described in a diffusive manner existing within a damage gradient or process zone. In a conventional fracture model, the crack exists in a discontinuous state, taking on a value of 0 or 1 (continuing the theme of damage) depending on whether the region is cracked or not. This is illustrated in Figure 28. The conventional crack exists in either broken (1) or unbroken (0) state, while the diffuse crack exists within a sharp damage gradient of length scale $\pm l$ that is continuous. It should be mentioned that in the foregoing discussion, the terms phase-field parameter is used interchangeably with damage parameter.

The mathematics behind PFM is quite complex, and therefore well outside the scope of the current document. Suffice to say that PFM offers advantages in both modeling accuracy, particularly with respect to HE damage, as well as certain numerical attributes that make it extremely attractive. As a result, several researchers have utilized PFM to tackle HE; including Martinez-Paneda et al. and Huang et al., [53]⁷[19].



Figure 28 Comparison of discontinuous crack and diffuse crack used in PFM

Phase-Field Model of Huang and Gao

The work by Huang and Gao is of particular interest in that they tackle fracture due to HE using phenomenological descriptions of *both* the HEDE as well as HELP mechanisms. It is valuable to review their study, reported in Reference [19] to illustrate the overall PFM method. In their work, they develop a framework addressing the range of behavior from brittle to ductile fracture resulting from HE. They define the damage variable, d, having values $0 \rightarrow 1$: $d \in (0,1)$. The damage function describing the diffuse field surrounding the crack is defined as,

$$g(d) = (1-d)^2$$
(17)

The damage function is then used to degrade both the elastic modulus as well as shrink the yield surface. The decrease in modulus effectively reduces the stiffness, and therefore the load bearing capacity of the structure. This results in the yield surface being a function of equivalent stress, damage, and equivalent plastic strain, $f(\sigma_e, d, \bar{\varepsilon}^p)$.

They employed a conventional approach to mass diffusion (lattice hydrogen) as outlined before following Sofronis and McMeeking [27]. The effect of strain on trapped hydrogen is addressed in a similar manner to Equation (9); however, in their work, the plastic strain is replaced by a function of plastic strain *and* the crack phase-field value.

The HELP mechanism is incorporated following Sofronis et al., and Liang et al., along the lines of Equations (15) and (16) where the yield surface is a function of equivalent stress, hydrogen concentration, damage, and equivalent plastic strain $f(\sigma_e, c, d, \bar{\varepsilon}^p)$. The HEDE mechanism is accounted for using the Griffith criteria of energy release rate as a function of hydrogen concentration, $\bar{G}_c = G_c(c)$. Where $G_c(c)$ is defined as follows:

$$G_c(c) = \begin{cases} \left[(\zeta - 1) \frac{c}{c_o} \right] G_c, & G_c(c) > \xi G_c \\ \xi G_c, & G_c \le \xi G_c \end{cases}$$
(18)

Here ζ and ξ control the reduction in the energy release rate, with ξG_c representing the lower bound. c_o is the initial concentration, while c is the concentration at any time. In their model, J_2 flow theory is used, and the deviatoric part of the stress tensor and the tensile part of the volumetric stress both degrade as the phase field (damage function) increases.

To summarize the model development, HELP is included in the phase-field model by shrinking the yield surface as function of hydrogen concentration, while HEDE is accounted for by reducing the energy-release rate required for fracture.

Analysis of Compact Tension Specimen

In the initial condition, the compact tension C(T) specimen starts out with a uniform hydrogen concentration throughout, and boundary conditions impose a closed system, i.e., no outgassing. Although chosen arbitrarily, the initial hydrogen concentration could be inferred from Sievert's Law assuming an environment containing a specific hydrogen partial pressure at a fixed temperature. The C(T) is loaded in displacement control at a suitably low strain rate to permit sufficient time for lattice diffusion to maintain a steady state during loading. The length scale of the diffuse phase (damage) field $(\pm l)$ is assumed to be 1 mm.

Results reproduced from Huang and Gao's work are shown in Figure 29 at a load just prior to crack formation and after some crack growth. The phase field values in shown in Figure 29(a), and the hydrogen concentration (shown in units of atoms/mm³) in Figure 29(b) are taken at the mid-section of the specimen at crack initiation. As expected, damage is concentrated at the root of the notch where both the stress and strain are also highest, and where hydrogen has accumulated. Recall that lattice hydrogen will diffuse to the region of high hydrostatic tensile stress. Figure 29(c) and (d) show results after some crack growth has taken place. Note in Figure 29(c) the diffuse damage zone surrounding the crack, where the region that is colored red had a damage value of 1 (cracked), surrounded by a steep damage gradient that would be expected in the wake of the crack. The maximum hydrogen concentrate at the crack tip and expands with increasing load (and time). The trapped hydrogen will also concentrate at the crack tip where the trap density is increasing with plastic strain. This is illustrated in Figure 30 showing the trapped hydrogen and total hydrogen after some crack growth.



Figure 29 PFM of C(T) specimen charged with hydrogen [19]





Simulations were performed to examine four cases to explore the effects of the two HE mechanisms incorporated in the model;

- 1. No HE,
- 2. HELP only,
- 3. HEDE only, and
- 4. Both HELP and HEDE.

The resulting load-displacement and plastic strain predicted from the simulated C(T) test of the four cases are shown in Figure 31.



Figure 31 Comparison of HE damage mechanisms in C(T) test simulations [19]

The calculated load-displacement curves are shown in the solid lines, and the plastic strain in dashed lines. Comparing Case 1 where no HE is included, with Cases 2 and 3 that incorporate HELP and HEDE respectively, show that the load bearing capacity and the fracture toughness are decreased. As expected, combining the two mechanisms, Case 4, shows the largest decrease in load-displacement and plastic strain. These results all show the expected behavior consistent with experimental results reported in the literature, as discussed previously. Other effects, like differences in time-dependency with and without HELP and HEDE, should show larger differences.

Analysis of Notched-Tensile Specimens

Huang and Gao also examined blunt notched bars to examine the impact of HE on a specimen with a macroscopic stress concentration⁺⁺. This is important to examine the model predictions for the effect of HE on damage that is not crack-like, i.e., dents, gouges, wrinkle bends, external corrosion patches, etc. Blunt notches are a common geometry to study influence of stress triaxiality $\left(\frac{\sigma_h}{\sigma_o}\right)$; here in relation to

both hydrogen distribution as well as damage development. It is known that increasing triaxiality (constraint) has a significant effect on fracture ductility. Increasing triaxiality has the effect of restricting plastic flow, leading to a reduction in fracture strain. It will also affect hydrogen distribution. Lattice hydrogen will be highest in the location of maximum hydrostatic stress. Increasing the plastic strain will increase the trapped hydrogen by increasing trap density. Therefore, both constraint and HE act in combination to accelerate damage, ultimately leading to crack formation and failure. Here the HELP and HEDE mechanisms compete for dominance. For example, a low-toughness material will fail at a lower energy release rate (stress intensity) and in such cases the HEDE mechanisms would dominate. High toughness materials, however, may be more affected by the effect of HELP, where the yield surface shrinks in relation to hydrogen concentration. In real cases, both mechanisms will exert some effect, and

⁺⁺ The reference to macroscopic stress is meant to distinguish the notch stress field from the local field around a sharp crack tip.

the phase field model is a very powerful way to explore this. A further note regarding the behavior of notch tensile bars should be made. For ductile materials with large fracture strain, damage will generally initiate at some distance from the notch root, while for brittle materials, fracture begins at the notch root. For ductile materials, failure is governed by void nucleation and growth is driven by the hydrostatic stress. If ductility is sufficiently high, the strain caused by the initial high principal stress at the notch root may be accommodated, permitting stress redistribution across the specimen thickness. If this is the case, ductile failure away from the notch root where the hydrostatic stress is highest. Alternatively, if the fracture strain is low, cracking will initiate at the notch root as the strain cannot be accommodated. This complex interplay between stress and strain field evolution as well as their influence on hydrogen concentration (and damage) make bars an ideal case to study.

In one set of simulations, Huang and Gao looked at the effect of energy release rate G_c on the fracture behavior of a flat offset double notched tensile bar. Varying G_c from low to high impacted the fracture behavior in a significant manner, as shown in Figure 32.





Figure 32 Damage in flat notch bars with varying critical energy-release rate G_c , [54]

In the low toughness case, $G_c = 0.8 \text{ mJ/mm}^2$, failure proceeds in a brittle manner largely dictated by HEDE. However, as the toughness increases to $G_c = 1.4$, the failure mode is now ductile linking the offset notches. At $G_c = 1$, there is a clear competition between failure modes.

Key Take-Aways

The application of computational damage mechanics (CDM)+ approaches for modeling HE represents a potentially valuable method in evaluating the effects of hydrogen on pipeline damage. Given the

experimental difficulty, generating test data in hydrogen is both costly and time consuming, especially in more complicated structural evaluations like a hot-tap or type B repair sleeve. Moreover, the challenges of performing full-scale validation tests require a major effort to obtain high-fidelity data while meeting the safety requirements posed by such an experiment. While small-scale test data are essential in calibrating numerical models, the use of simulated full-scale experiments offers the potential to explore many different forms of damage ranging from cracks to dents, of varying degrees of severity. To be clear, full-scale testing is a necessary step in validating the numerical CDM methods, but once sufficient validation has been performed, these models can be used to perform fitness for service analyses to help determine the feasibility of repurposing a pipeline for hydrogen service. In the interim, CDM may be used to assess the relative effects of HE on pipeline integrity. The PFM appears to offer significant advantages due to the more realistic phenomenological approach to modeling the HELP and HEDE mechanisms. The ability to explore damage development without a pre-determined crack path or failure mode is powerful in better predicting the structural integrity limits of real structures like pipelines.

Evaluating the Repurposing Vintage Pipelines to Hydrogen

In the preceding discussion, two alternatives were presented as methods for evaluating damage, and ultimately modeling defects in pipelines. One of the aims of this project is to evaluate various types of damage and compare the relative difference in defect tolerance with and without hydrogen. Based on test data of vintage pipelines steels in hydrogen outlined in Reference [6], it is clear tolerance to certain defects will decrease once hydrogen is introduced into NG (or 100% hydrogen). For example, loss in fracture toughness will reduce the critical flaw size. The fatigue crack growth rate is also higher in hydrogen compared with nitrogen. Meng et al. performed a similar study looked at the effects of FCGR on an X80 steel in various hydrogen blends [55]. They showed a significant increase in growth rate with the introduction of 5 vol% H₂. Further increases in hydrogen increased the growth rate, but not significantly different than the initial introduction of H₂. Their Paris Law coefficients are shown in Table 2 (mm/cycle, MPa-Vm).

Added hydrogen /vol%	0	5	10	20	50
С	2.259E-8	2.495E-7	2.877E-7	3.304E-7	4.613E-7
m	2.59	2.59	2.59	2.59	2.59

 Table 2
 Paris Law coefficients for fatigue crack growth rates from Meng et al. [55]

Using these coefficients, an example fatigue crack growth calculation was made assuming a 0.5-mm deep axial flaw with a 3:1 aspect ratio in a pipe with 1,000 mm diameter and 15-mm wall thickness. The pressure cycle is assumed to be a constant ΔP of 10 MPa. The results are shown in Figure 33.



Figure 33 Fatigue crack growth calculation

This example suggests the fatigue life in hydrogen is about 30% of a nitrogen (or NG) environment with an existing axial surface crack, although there is the time to crack initiation as well.

Directionally, loss in fracture strain suggests that damage such as dents, wrinkle bends, or axial strains from external forces may be more prone to cracking in hydrogen service. A related question regards the differences in behavior of existing damage, or damage that is caused after introduction to hydrogen. Data from Dutkiewicz et al., looking at the effect of pre-strain on stress-strain curve showed a progressive loss in fracture ductility with increasing pre-strain [34]. Although there could be a decrease in life from fatigue crack initiation for new pipelines.

The data seems to indicate that tensile pre-straining the test specimen enhances hydrogen uptake resulting in fracture at a lower strain. Another factor affecting pipelines containing dents or gouges is the fatigue life. Data have shown that the endurance limit is also diminished in hydrogen [56]. Under lowcycle fatigue, the number of cycles to crack formation is closely related to the fracture strain. It has also been shown that in testing notched tensile bars, the notch acuity affects the stress to fracture [57]. Taken together, these factors may require more stringent repair criteria for certain types of defects. However, fitness for service procedures for dents or gouges are largely based on empirical rules. Pluvinage et al., looked at the potential implications for plain dents in terms of the EPRG criteria [58] [59]. The EPRG criteria indicates that dent depths up to 7% (for a pressurized pipe) will not crack at membrane stresses below 72% SMYS. Using the procedure from Oyane et al., which is a ductile fracture model based on void growth and coalescence [60]. Assuming a uniaxial failure strain of 23% in hydrogen, the maximum damage was found at 4% dent depth. For a failure strain of 31.5% in air, the maximum damage was predicted to be about 6%. It should be noted that this damage model does not explicitly address HE; rather, the uniaxial fracture strain is adjusted by test data as well as a constraint factor accounting for the geometry. To investigate the effects of dents or other damage, it is desirable to incorporate a phenomenological description of the damage process.

An important question will be the potential for cracking at hard spots. These are local spots of untempered martensite with a high hardness and tensile strength, but poor ductility and toughness. Failures have occurred that were attributed to hydrogen charging (from cathodic protection systems, loss of coating, and deleterious soil conditions) at these locations. This is a complex topic, and difficult to simulate using full-scale tests. From a modeling standpoint, accounting for the local stress and strain associated with the hard spot after rolling pipe with the thermal-plastic/phase-transformation induced residual stresses is a challenging task. Due to the potential integrity threats, they pose, testing as well as analysis will be needed to determine the magnitude of this issue. However, it is interesting to note that the hydrogen flux can be much larger from the corrosion process of pipe without an external coating than from gaseous exposure and may actually be a more bounding condition. The external hard spot failures in NG/oil lines, however, require that there is damage to the external coating; while the gaseous hydrogen could affect even hard spots with good coating.

Directions for the Current Project

A key deliverable in this project is the predicted behavior of pipeline damage in hydrogen service. To address this, PFM has been chosen as the analysis methodology for the reasons outlined in previous sections. Numerical simulations will be used to examine several common defect types such as axial seam cracks, localized metal loss, dents, wrinkle bends, and possibly others. Material property data will be taken from the literature for relevant pipeline steels. Parametric studies will look at different defect geometries and various hydrogen concentrations. It is expected that the results will provide insight into the feasibility of converting existing pipelines from NG to hydrogen, and if so, under what conditions. At a minimum, such work will provide guidance on suggested full-scale testing to be developed in a companion DOT/PHMSA project being conducted by Emc².

Preliminary Work Results

Initial scoping work looked at hydrogen distribution in a local thin area on a corroded pipe and a dent subject to hydrotesting at two pressures. This was not done using PFM but rather with existing Abaqus features with simpler predictions of the hydrogen concentrations and is shown here for illustrative purposes only.

Corroded Pipeline

The geometry of the corroded region from a laser scan of a pipe is shown in Figure 34, which came from work on a prior DOT/PHMSA.



Figure 34 External corrosion profile on pipeline

In Step 1, an initial boundary condition was established such that the ID surface of the pipe wall had a hydrogen concentration of 2.5 ppm, and the zero at the OD. Next, the pipe was pressurized and held for a sufficient time to establish a steady-state hydrogen concentration. Following this, two cases were run; the first involved a hydrotest to 72% SMYS, and the second to 125% SMYS. After each step the pressure was returned to the original operating pressure. The results are shown in Figure 35.



Figure 35 Hydrogen concentration in pipeline wall

There is a noticeable difference in the hydrogen concentration profile following hydrotest. Recall that the lattice hydrogen solubility is a function of hydrostatic stress, and therefore as the pipeline is pressurized, resulting in local yielding, stress redistribution takes place and affects the local concentration of hydrogen. *In this example calculation, only the lattice hydrogen is accounted for, and the effect of hydrogen trapping caused by plastic strain is not considered.*

Dented Pipeline

Another example looked at the effect of hydrotesting on a dented pipeline. Again, the same boundary conditions for hydrogen concentration were used. A rigid indenter was used to create a dent having a peak plastic strain of about 15%. In this case, the two hydrotests were conducted at 125% and 187% of SMYS. The equivalent plastic strain is shown in Figure 36.



Figure 36 Pipeline with dent showing equivalent plastic strain PEEQ

The initial hydrogen concentration after pressurizing to operating and following the two hydrotests are shown in Figure 37.



Figure 37 Hydrogen profile in dented pipeline following hydrotesting

In this example, the hydrogen distribution is considerably changed following each hydrotest. For both examples, it could be inferred that the application of a hydrotest could have an adverse effect on structural integrity. To determine this, however, the effects of HE need to be incorporated into the model, as well as the impact of trapped hydrogen. These areas are currently being studied as part of this program using PFM. The effects of hydrogen on damaged pipelines will be compared to current NG service to assess the relative impact of repurposing to hydrogen.

Summary

Use of existing NG transmission pipelines, or at least a significant portion, will be needed to transport hydrogen. The steps that may be required to repurpose NG are not yet clear and require additional study in terms of physical tests as well as engineering analysis. At the current time, small-scale data on materials properties is currently being developed at a rapid pace. However, full-scale test data needed for validation of engineering models remains scarce. In the near term, use of numerical modelling techniques, in conjunction with small-scale mechanical test data, can provide insight into the impact of repurposing NG lines to hydrogen, and in determining the safe operating envelope. A promising approach for modeling HE of pipelines with various forms of damage is the phase-field method (PFM). This technique can provide coupled analysis of mass diffusion and stress-strain analysis to track damage evolution. Recent work by Huang and Gao has provided the groundwork for applying PFM to this problem. Work as part of this program will use advanced analysis tools such as PFM to examine the safe operating conditions of vintage pipelines used to transport hydrogen. Integrity limits will be compared to the existing NG service to develop relative trends. Key questions such as the crack tolerance, impact on acceptable strain limits of dents or wrinkle bends, and acceptance of locally corroded areas will all be examined.

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