HYDROGEN COMPATIBILITY OF STRUCTURAL MATERIALS IN NATURAL GAS NETWORKS

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ABSTRACT

There is growing interest in utilizing existing infrastructure for storage and distribution of hydrogen. Gaseous hydrogen, for example, could be added to natural gas in the short-term, whereas entire systems can be converted to transmission and distribution networks for hydrogen. Many active programs around the world are exploring the safety and feasibility of adding hydrogen to these networks. Concerns have been raised about the structural integrity of materials in these systems when exposed to hydrogen. In general, the effects of hydrogen on these materials are grossly misunderstood. Hydrogen unequivocally degrades fatigue and fracture resistance of structural steels in these systems, even for low hydrogen partial pressure (~1 bar). In most systems, however, hydrogen effects will not be apparent because the stresses in these systems remain very low. Another misunderstanding results from the kinetics of the hydrogen effects: hydrogen degrades fatigue and fracture properties immediately upon exposure to gaseous hydrogen, and those effects disappear when the hydrogen environment is removed, even after prolonged exposure. There is also a misperception that materials selection can mitigate hydrogen effects. While some classes of materials perform better in hydrogen environments than other classes, for most practical circumstances, the range of response for a given class of material in gaseous hydrogen environments is rather narrow. These observations can be systematically characterized by considering the intersection of materials, environmental, and mechanical variables associated with the service application. Indeed, any safety assessment of a hydrogen pressure system must quantitatively consider these aspects. In this report, we quantitatively evaluate the importance of the materials, environmental, and mechanical variables in the context of hydrogen additions to natural gas piping and pipeline systems with the aim of providing an informed perspective on parameters relevant for assessing structural integrity of natural gas systems in the presence of gaseous hydrogen.

1.0 INTRODUCTION

As decarbonization has become a priority in many parts of the world, greater attention has been given to decarbonize sectors such as natural gas networks. The options to eliminate carbon from natural gas are rather limited, as removing carbon leaves only hydrogen. There may be carbon-neutral ways to manage gas networks, but hydrogen may be the only method to eliminate carbon in the network. Currently, the hydrogen supply chain cannot replace natural gas, therefore, transition strategies are being considered, such as adding hydrogen in relatively small quantities to existing infrastructure. This concept is usually referred to as ‘blending’.

The amount of hydrogen being considered in networks around the world depends principally on regional regulation and ranges from a few percent to as much as 20% [1]. One primary concern for addition of hydrogen to natural gas networks is the end-user appliances, as hydrogen changes the flame speed and performance of burners in typical appliances. Consequently, in the short-term, hydrogen blending will likely be limited to concentrations less than 15-20%. The effect of hydrogen on the network itself is also an important consideration, since hydrogen embrittlement is a known phenomenon that degrades the ductility properties of structural metals. While the concept of hydrogen embrittlement is well known, the details of hydrogen embrittlement are generally misunderstood.

In this brief report, we summarize the general principles of hydrogen embrittlement in the context of structural steels used for piping and pipelines in natural gas networks. The effects of hydrogen are considered in the context of the materials, environmental and mechanical variables that contribute to hydrogen embrittlement of structural metals. Deconstruction of the embrittlement problem into these three components provides a framework to understand and manage the effects of hydrogen in structural metals, since all steels are embrittled by hydrogen, including at low pressure and low concentrations of hydrogen [2]. To this end, data from the literature are used to draw general conclusions about hydrogen embrittlement in gas networks; however, we also provide a brief description of general procedures for measuring relevant fatigue and fracture design properties in gaseous hydrogen environments.

2.0 EXPERIMENTAL PROCEDURES

2.1 Materials

For the purposes of this report, we focus on transmission line pipe steels, essentially API grade pipeline steels designated as X52, X60, etc., where the number refers to the specified minimum yield strength in units of ksi. Materials pedigree is essential to understanding environmental effects. Compositional and microstructural variables can be important, in some cases, and may be particularly important for steels made more than 50 years ago. The steels reported here are mostly 'modern' steels representing high-quality materials with a range of ferritic microstructures [3]. For these 'modern' steels, the microstructural characteristics are indicative of the strength of the steel with only modest differences in composition.

2.2 Hydrogen environment

Design data for hydrogen service should always be evaluated in situ in a relevant gaseous environment. This is required by the ASME B31.12 Code [4]. The effects of gaseous hydrogen are generally reversible, meaning if the hydrogen environment is removed the material will recover its (non-exposed) properties. Additionally, pipeline steels are characterized be rapid hydrogen diffusion, thus hydrogen can diffuse out of the material on the time scale of minutes when the hydrogen environment is removed, see discussion below. Therefore, a procedure of pre-exposing materials to gaseous hydrogen, removing from the hydrogen environment and then testing in air does not provide a known hydrogen condition, and should not be used for design or fitness-for-service determination. Comprehensive testing protocols for evaluating fatigue and fracture behavior in gaseous hydrogen environments are provided in the ANSI/CSA CHMC1 standard [5]. Small quantities of air (or other impurities) can compromise testing, thus care should be taken to verify the quality of the hydrogen environment by testing the gas from the environmental test system. The composition of the source gas is not sufficient to ensure the quality of the testing environment since the test gas will always have greater impurity content than the source gas.

Both the total system pressure and the hydrogen partial pressure are necessary to establish the relevant thermodynamic boundary conditions for hydrogen in equilibrium with a metal. The thermodynamic activity of hydrogen is determined from the hydrogen fugacity (the thermodynamic pressure), which requires knowledge of both the total system pressure and the hydrogen partial pressure [2, 6]. For the purposes, of this report, we consider mostly testing in pure gaseous hydrogen with impurity content consistent with the requirements of the ANSI/CSA CHMC1 standard: oxygen and moisture content less than 5 and 10 wt ppm respectively [5]. An example of hydrogen in nitrogen is also considered, characterized by the total pressure and the percentage of hydrogen (by volume).

2.3 Fracture mechanics measurements

Performance-based design methodology for pressure piping (such as described in ASME B31.12) consists of two principal materials characteristics: fatigue crack growth and fracture toughness. These properties are used in fracture mechanics-based design and fitness-for-service assessments. Both properties can be evaluated from multiple test geometries, but in the context of hydrogen-assisted fatigue and fracture, the majority of testing has been performed with the compact tensile (CT) geometry [7]. With proper test design, both properties can be evaluated from the same test specimen for most ductile metals.

ASTM E647 provides a standardized test method for fatigue crack growth, which can be adopted for testing in gaseous hydrogen as discussed in the ANSI/CSA CHMC1 standard [5]. Several international standards describe methodologies for determining fracture toughness, although ASTM E1820 provides perhaps the most comprehensive and general description of the methods for determination of elastic-plastic fracture toughness (e.g., J_{IC}). For low-strength, ductile metals, elastic-plastic fracture methods are generally needed to determine valid plane-strain fracture toughness in gaseous hydrogen; therefore, the methods in ASTM E1820 have typically been employed in the literature for determining fracture resistance in hydrogen environments (fracture resistance is used throughout this report, in place of fracture toughness, to emphasize the environmental dependence of the measurement). The ASME B31.12 Code refers to the constant displacement (or load) method in ASTM E1681 for determination of the crack arrest threshold; however, there are several challenges employing this methodology to determine quantitative values of fracture resistance of ductile metals as described in Refs. [8, 9]. For the purposes of this discussion, the fracture resistance implies the ASTM E1820 methods or equivalent in which a rising displacement fracture test is conducted in-situ a gaseous hydrogen environment.

Tensile properties are an important element of characterizing materials of construction for structural applications. Tensile properties, for example, are used to characterize plastic collapse in fitness-for-service assessments. However, tensile properties do not quantitatively characterize fatigue and fracture failure modes. In general, hydrogen reduces tensile ductility properties such as elongation and reduction of area, but hydrogen does not affect tensile strength properties in pipeline steels [10]. Therefore, for the purposes of structural integrity assessment for hydrogen service, tensile testing in hydrogen environments is generally not necessary if fracture mechanics is the design basis for the structure.

3.0 RESULTS

Fatigue crack growth is typically presented as a plot of fatigue crack growth rate (*da/dN*) as a function of stress intensity factor range (ΔK). The quantity *da/dN* represents crack extension per load cycle, or in the case of pressure loading, per pressure cycle. The quantity ΔK is a fracture mechanics term that reduces the geometry, applied load (pressure in this case) and size of a crack into a single parameter that is used in design and fitness-for-service assessment. In general, the *da/dN*-ΔK of most steels can be represented over the relevant range of ΔK by a simple power law of the form: $da/dN = C(\Delta K)^m$.

Typical fatigue crack growth curves are shown in Figure 1 for testing performed in high-pressure pure gaseous hydrogen, compared to tests in air. Most pipeline steels show similar fatigue crack growth behavior in air. As shown in Figure 1a, a diverse range of pipeline steels show similar behavior in gaseous hydrogen for the same testing conditions. As shown in this figure, at low ΔK, the fatigue response in hydrogen appears to converge with the behavior in air, whereas at high ΔK fatigue crack growth in hydrogen is greater than in air by a factor of more than 10. Figure 1b shows fatigue crack growth response of several different alloy designs of X80 steel; all with similar behavior. The fatigue crack growth is furthermore characterized by a transition or knee in the fatigue crack growth response, which can be idealized as two separate power laws: at low ΔK, the power slope (m) is almost twice the value at high ΔK. At high ΔK, the fatigue crack growth curve is approximately parallel to the curve in air. The dashed lines in both figures represent this idealized two-part power law as described by the equations in section 4.2 and Ref. [11].

The fatigue response of pipeline steel in gaseous hydrogen at low partial pressure shows similar behavior as in high-pressure hydrogen as shown in Figure 2 for data from Ref. [2]. In the case for hydrogen partial pressure of approximately 1 bar (one atmosphere), the crack growth response in the high ΔK regime is similar to the rate at high pressure. At low ΔK, however, the crack growth rate in low-pressure hydrogen is somewhat lower than at high pressure.

The fracture resistance in high-pressure gaseous hydrogen is shown in Figure 3a as a function of tensile strength for a range of line pipe steels. In general, for these steels, the fracture resistance in hydrogen scales approximately with the strength of the material. The effect of hydrogen fugacity on fracture resistance is shown in Figure 3b. The fracture resistance shows a steep dependence on hydrogen fugacity at low hydrogen pressure with a decaying dependence at high pressure, indicative of a negative power law dependence on the fugacity [2].

4.0 DISCUSSION

4.1 Materials variables

The fatigue crack growth of API 5L steels in gaseous hydrogen appears to be remarkably insensitive to grade and microstructure of the steel, at least for the steels shown in Figure 1. These steels represent a range of microstructures from ferrite-pearlite (X52 [12]) to polygonal ferrite (X60 [3, 7]) to acicular ferrite (X80 [3, 13]) to largely bainite (X100 [14]). In short, hydrogen has a substantial effect on fatigue crack growth of line pipe steels without regard for the microstructural details within the ranges summarized here.

Fracture resistance in hydrogen shows a little more variability between alloys than fatigue crack growth (Figure 3a). The fracture response appears to scale nominally with the strength of the alloy. Conventional, modern alloys (yield strength $\leq$ 600 MPa) show fracture resistance greater than 55 MPa m$^{1/2}$ for hydrogen pressure up to 21 MPa [7, 13, 15], whereas higher strength grades (i.e., X100) can drop below this value [14]. Vintage steels from before the 1970s have not received as much attention with regard to testing in gaseous hydrogen, but the few examples in the literature are consistent with Figure 3a [16].

4.2 Environmental variables

For the purposes of this study, we do not consider the effect of oxygen and other impurities that may be present in natural gas. Oxygen can mitigate the effects of hydrogen for some conditions; however, it is important to consider that the efficacy of oxygen depends on numerous factors and disappears when oxygen cannot outcompete hydrogen for surface sites at a crack tip (e.g., at high fatigue crack growth rates where the effect of hydrogen is recovered) [12]. Notably, the effect of oxygen also depends on the concentration of oxygen, therefore, different sources of natural gas may result in different response for the same hydrogen partial pressure. Consequently, it is difficult to draw general conclusions for the effects of hydrogen when gaseous mitigators are present. Rather, we focus on the effect of low-pressure hydrogen considering the natural gas as an inert component in the gas blend.

Meng at al. showed that the fatigue crack growth in hydrogen-inert gas mixtures with 5 to 50% hydrogen is effectively independent of the hydrogen concentration [17]. Their results were biased to ΔK > 30 MPa m$^{1/2}$, but the fatigue crack growth rates are coincident with the upper ΔK regime in Figure 2. The upper ΔK regime (above the knee) appears to be independent of pressure as the same power law characterizes pressure vessel steels in hydrogen at pressure of 1060 bar [11]:

$$\frac{da}{dN}\lfloor\mathrm{m/cycle}\rfloor = 1.5\times10^{-11}\left(\frac{1+2R}{1-R}\right)\Delta K^{3.66}$$

where R is the load ratio. The lower ΔK regime, on the other hand, displays pressure dependence, which follows a square root dependence of hydrogen fugacity of the form [11]:

$$\frac{da}{dN}\lfloor\mathrm{m/cycle}\rfloor = 3.5\times10^{-14}\left(\frac{1+0.4286R}{1-R}\right)\Delta K^{6.5}\left(\frac{f}{2110}\right)^{1/2}$$

where f is the fugacity of the hydrogen (in units of bar) and 2110 is the fugacity of hydrogen at the reference pressure of 1060 bar. The dashed lines in Figures 1 and 2 derive from these two power law relationships (the knee corresponds to the ΔK at which these two relationships are equal). The scaling of the crack growth rate at low ΔK was proposed empirically [11], but it is based on thermodynamic equilibrium since the concentration of hydrogen in the metal is proportional to the square root of the hydrogen fugacity [18]. In short, while the effects of hydrogen on fatigue crack growth depend on several factors, a substantial increase in fatigue crack growth rates are apparent even for hydrogen partial pressure as low as 1 bar (Figure 2). At high crack growth rates, fatigue crack growth is effectively independent of pressure for hydrogen partial pressure between 1 bar and 210 bar as shown in Figure 2 (and as high as 1060 bar if data for pressure vessel steels is considered [11], although not shown here).

Hydrogen partial pressure less than 1 bar has been shown to have a significant effect on fracture resistance of an X70 pipeline steel [19]. In a separate study, a higher partial pressure was necessary to achieve a large reduction of fracture resistance for an X52 pipeline steel, but represented a single test [2]. The difference in these two studies may result from the steep dependence on fugacity at low values (i.e., negative square root dependence) or possibly a role of impurities in the latter case. Both a negative square dependence [13] and a negative fourth root dependence [2] have been proposed, depending on which fracture parameter is assumed to scale with fugacity (since $K \propto \sqrt{J}$). Again, these dependencies arise from an assumption that one of these fracture properties scales linearly with hydrogen concentration within the metal, which at thermodynamic equilibrium is proportional to the square root of the fugacity. Figure 3b provides some overview of the effect of pressure and clearly even low partial pressure hydrogen can have an effect. More data are necessary to establish appropriate scaling of fracture resistance with pressure/fugacity. Additionally, it should be noted that percentage of hydrogen in natural gas is not sufficient information to describe the hydrogen environment. The thermodynamic pressure, or fugacity, is the physically meaningful parameter that is needed to characterize equilibrium hydrogen content in metals; therefore, the fugacity (or partial pressure) of hydrogen is a more relevant characterization of the environment than the percentage of hydrogen in a gas blend.

4.3 Mechanical variables

The mechanical variables that affect fatigue and fracture include testing variables, such as fatigue frequency, fatigue load ratio (R), and loading rate. Considering the diffusion rate of hydrogen in iron (~1.6×10^{-4} cm^2/s at room temperature [20]), exposure time in hydrogen is unlikely to have a substantial effect on fatigue and fracture measurements. This diffusivity (D), for example, corresponds to diffusion distances (x) on the order of one centimeter per hour ($x \sim \sqrt{4Dt}$, where t is time). Since the relevant material volume is very near the crack tip (microns) in a fracture mechanics test, the effects of hydrogen can be manifested almost immediately without a need for soaking the test specimen in the gaseous environment. Even on the time scale of a single fatigue cycle, hydrogen transport can keep pace with a growing fatigue crack over the typical range of fatigue crack growth rates (Figure 1) and for frequency as high as 1 Hz. These times scales additionally imply that hydrogen can leave the specimen rapidly, thus testing in air after exposure to hydrogen is unlikely to result in a known boundary condition for hydrogen. In other words, meaningful evaluation of the effects of gaseous hydrogen must be performed *in situ* in the hydrogen environment.

5.0 CONCLUSIONS

Assessing the general trends of measured fatigue and fracture properties of transmission pipe steels in gaseous hydrogen environments, the following conclusions can be drawn:

- Materials variables
    - Modern line pipe steels display similar fatigue crack growth behavior in gaseous hydrogen for typical grades from X52 to X80, including experimental grades of X100.
    - Fracture resistance in gaseous hydrogen nominally scales with strength properties.
- Environmental variables
    - At low ΔK, fatigue crack growth approximately scales with the square root of hydrogen fugacity.
    - At high ΔK, fatigue crack growth is approximately independent of hydrogen fugacity; in other words, fatigue crack growth in hydrogen at partial pressure of 1 bar is the same as in hydrogen at pressure of 210 bar (and potentially much higher pressure).
    - Fracture resistance nominally scales with square root of hydrogen fugacity.

    - It is fundamentally incorrect to assert that hydrogen has no effect below some threshold concentration in a blended gas.
- Mechanical variables
    - Kinetics of hydrogen transport in ferritic steels is rapid and generally does not limit fatigue and fracture testing as long as those tests are performed *in situ* in a gaseous hydrogen environment.

From a materials perspective, hydrogen unequivocally degrades the structural performance of pipeline steels and without known exception. In general, however, pipeline steels remain ductile in hydrogen environments, even though fatigue crack growth is accelerated, and fracture resistance is degraded. From a structural integrity perspective, however, materials degradations may not change the operational performance of the system, see Ref. [2]. The implication of hydrogen-assisted fatigue and hydrogen-assisted fracture must be assessed for the structural and operational characteristics of any given pipeline, as fitness for service will depend on the intersection of materials performance, environmental conditions, and the applied stresses.

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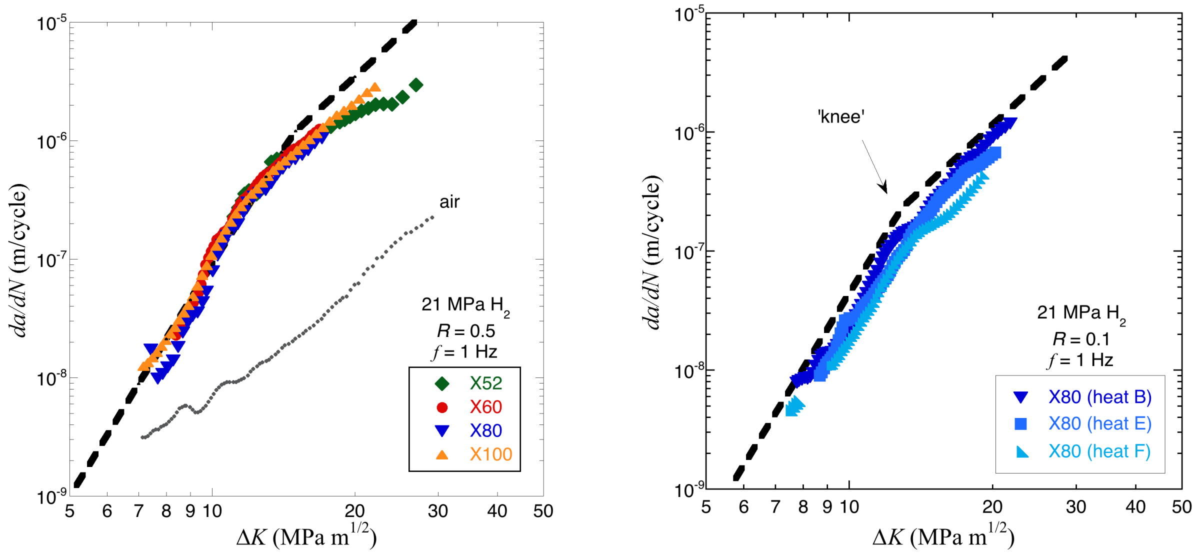


(a) (b)

Figure 1. (a) Fatigue crack growth curves for API 5L steels in pure gaseous hydrogen at pressure of 21 MPa and load ratio R = 0.5. (b) Fracture resistance of three heats of X80 grade steel in pure gaseous hydrogen at pressure of 21 MPa and load ratio of R = 0.1. Dashed lines represent power law curves from the text for pure hydrogen at pressure of 21 MPa.

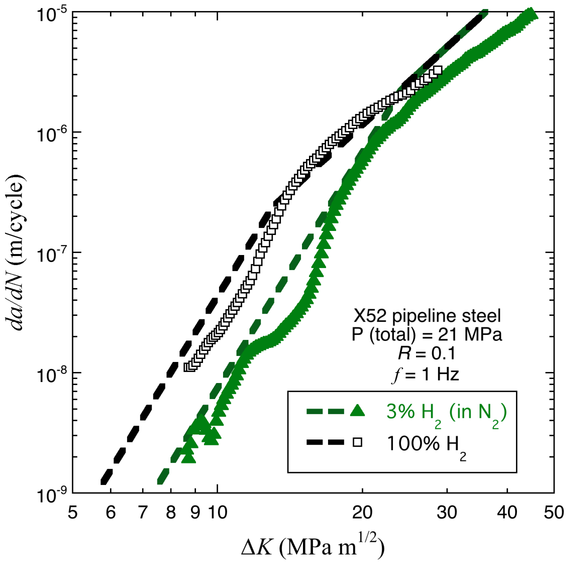
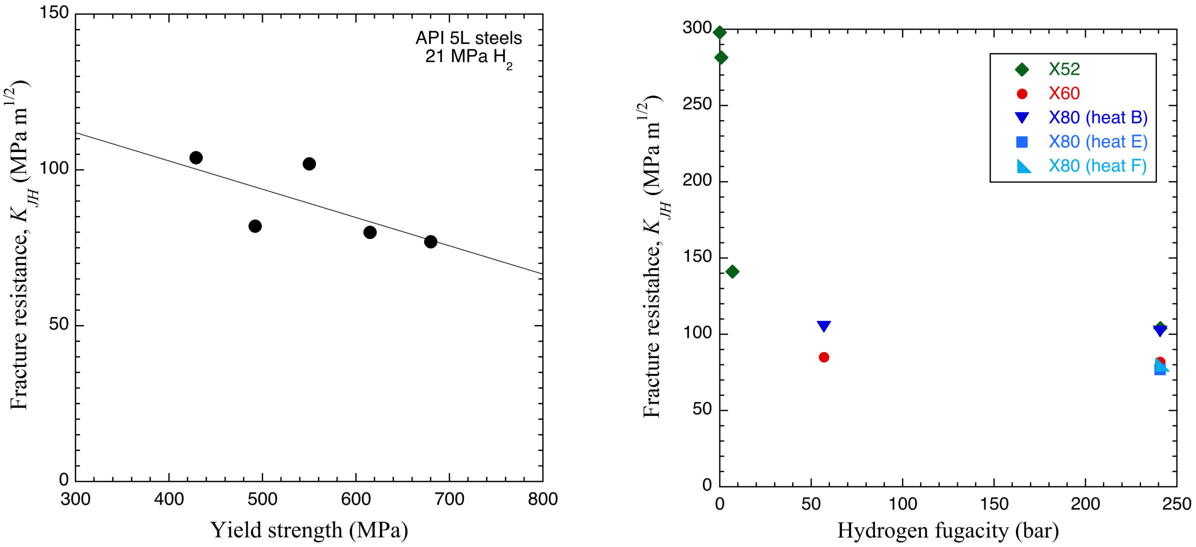


Figure 2. Fatigue crack growth curve of X52 grade steel in nitrogen with 3% by volume hydrogen and in 100% hydrogen at total pressure of 21 MPa. Dashed lines represent power law curves from the text for the fugacity of hydrogen in the two conditions respectively.



(a) (b)

Figure 3. (a) Fracture resistance of API 5L steels in pure gaseous hydrogen at pressure of 21 MPa. (b) Fracture resistance of API 5L steels as a function of hydrogen fugacity.