HYDROGEN EFFECTS ON X80 PIPELINE STEEL UNDER HIGH-PRESSURE NATURAL GAS/HYDROGEN MIXTURES

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ABSTRACT
Blending hydrogen into the existing natural gas pipeline has been proposed as a means of increasing the output of renewable energy systems such as large wind farms. At present, X80 pipeline steel is commonly used for transporting natural gas. However, the pipeline steel is subjected to concurrent hydrogen invasion with mechanical loading while being exposed to hydrogen containing environments directly, and then hydrogen embrittlement (HE) of metals may occur. In accordance with ASTM standards, the mechanical properties of X80 pipeline steel have been tested in natural gas/hydrogen mixtures with 0, 5.0, 10.0, 20.0 and 50.0vol% hydrogen at the pressure of 12MPa. The results indicate that X80 pipeline steel is susceptible to hydrogen-induced embrittlement in natural gas/hydrogen mixtures and the HE susceptibility increases with the hydrogen partial pressure. Additionally, the HE susceptibility depends on the texture microstructure caused by hot rolling, especially for the notch specimen. From the designed life calculation by the measured fatigue data, it is found that the designed life of the X80 steel pipeline is degraded by the added hydrogen dramatically.

Keywords: X80 pipeline steel; HE; mechanical properties; natural gas/hydrogen mixtures; designed life

1.0 INTRODUCTION
A series of progressive decrease in the reserves of fossil fuels and environmental problems associated with burning them have promoted the search for alternative energy, including renewable energies. Wind power is the renewable energy with the greatest potential so far. Regarding the wind energy production, global wind power installed capacity grew to 369.55GW in 2014. Nevertheless, the uncertainty associated with wind generation related to the wind speed variability and intermittence causes the mass waste of wind power. Hydrogen has been regarded as a promising energy carrier for renewable energy sources for a long time [1-2]. Using the excessive wind power to produce hydrogen by water electrolysis ranks high in terms of technical and economical feasibility, which has a great potential to increase the output of wind power as well as to improve the environment [3-5]. Meanwhile, concerning the huge amounts of electrolytic hydrogen transportation, blending hydrogen into the existing natural gas pipeline is a famous solution which could provide major cost/schedule benefits.

The existing natural gas system has been designed for natural gas, the impact of the presence of hydrogen on the pipeline materials should be studied because most high pressure (generally between
3.5MPa and 8.4MPa) gas pipelines are composed of ferritic steels, which are known to be more susceptible to HE [6,7]. The study of hydrogen embrittlement (HE) in the high-pressure natural gas/hydrogen mixtures have been studied [8]. Previous research works indicate that the HE effect is dependent on the type of steel and the amounts of added hydrogen [9-11]. These studies mostly analyze the effect of hydrogen on pipelines only for material itself. The studies about fracture mechanics calculation which is based on the experimental data in hydrogen containing environment are scarce.

In this paper, the mechanical properties of X80 pipeline steel have been investigated in natural gas/hydrogen mixtures with 0, 5.0, 10.0, 20.0 and 50.0% hydrogen at the pressure of 12MPa initially, and then the degradation of the mechanical properties is analyzed from the aspects of the specimen types, the material microstructure and the amounts of added hydrogen. Finally, a fracture mechanics based approach have been applied to calculate the designed life of an example pipeline to estimate the effect of hydrogen.

2.0 EXPERIMENTAL

2.1 Test equipments

An INSTRON hydraulic servo controlled testing machine with an autoclave was used to measure the mechanical properties in natural gas/hydrogen mixtures. The autoclave has the high resistance to HE with a capable of holding hydrogen gas pressures up to 20MPa. The testing machine is designed for normal mechanics tests in various gas environments.

2.2 Specimen preparation

Tensile and fatigue crack growth tests were conducted in high-pressure natural gas/hydrogen mixtures on specimens taken from API-5L steel grades X80. Figure 1 shows the specimen geometries. The tensile specimens were cut from along the longitudinal of the pipeline and the Compact Tensile specimens with fracture surfaces perpendicular to the longitudinal were used for the fatigue crack growth tests. The surface of all specimens were mechanically polished with a 2000 grade SiC paper and then cleaned ultrasonically in acetone.
Figure 1. Specimen geometry of smooth tensile specimen (a), notch tensile specimen (b) and Compact Tensile specimen (c)

2.3 Material

The chemical composition of X80 steel studied here is given in Table 1. It was received from an ingot after a regulated two-stage hot-rolling process. The initial rolling temperature was 1050°C and followed by the rolling temperature of 850°C.

<table>
<thead>
<tr>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Nb</th>
<th>V</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Ti</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.061</td>
<td>1.81</td>
<td>0.28</td>
<td>0.062</td>
<td>0.058</td>
<td>0.03</td>
<td>0.03</td>
<td>0.22</td>
<td>0.15</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

2.4 Environment

Methane is the primary component of natural gas, to minimize the effect of impurities and ensure the safety, nitrogen gas was used to replace natural gas, which is known as stable as methane at ambient temperature. Experiments were conducted at a pressure of 12MPa at ambient temperature in 0, 5.0, 10.0, 20.0 and 50.0 vol% hydrogen blends, corresponding to hydrogen partial pressure of 0, 0.6, 1.2, 2.4 and 6.0MPa, respectively. Pressurization and system purging was conducted before testing: through (1) pressurization with dry nitrogen gas, (2) evacuation and (3) pressurization with the pure hydrogen and nitrogen gas.

3.0 EXPERIMENTAL RESULTS

3.1 Tensile properties

Tensile testing is the most ubiquitous material property measurement technique which is used extensively for characterizing HE, and it is a useful screening method for materials in hydrogen gas service. In this study, slow strain rate tests (SSRT) were performed on the smooth and notch specimens which were taken from X80 steel in order to obtain the mechanical properties like ultimate tensile strength, yield tensile strength, notch tensile strength, elongation and reduction of area, which conformed to ASTM standard G142. The strain rate was 0.05mm/min for smooth tensile specimens and 0.01mm/min for notch tensile specimens.

3.1.1 Smooth tensile properties
The influence of hydrogen concentration on the tensile behavior of the smooth specimens is shown in Figure 2, the corresponding tensile data is given in Table 2. The results indicate that the added hydrogen has no effect on the ultimate tensile strength as well as the strain hardening step preceding necking. On the contrary, a decrease of the elongation and the reduction of area are observed with increasing hydrogen.

![Figure 2](image_url)

**Figure 2. Influence of the added hydrogen on the tensile properties of the smooth tensile specimens**

<table>
<thead>
<tr>
<th>Added hydrogen vol%</th>
<th>Ultimate tensile strength MPa</th>
<th>Yield tensile strength MPa</th>
<th>Elongation %</th>
<th>Reduction of area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>656.39</td>
<td>523.90</td>
<td>26.88</td>
<td>77.77</td>
</tr>
<tr>
<td>5</td>
<td>666.00</td>
<td>518.56</td>
<td>24.58</td>
<td>75.13</td>
</tr>
<tr>
<td>10</td>
<td>657.81</td>
<td>525.52</td>
<td>23.85</td>
<td>74.41</td>
</tr>
<tr>
<td>20</td>
<td>656.06</td>
<td>524.83</td>
<td>22.19</td>
<td>65.42</td>
</tr>
<tr>
<td>50</td>
<td>661.54</td>
<td>523.67</td>
<td>21.91</td>
<td>64.73</td>
</tr>
</tbody>
</table>

The corresponding fractographs of the specimens are presented in Figure 3. To quantify the influence of hydrogen, an embrittlement index $E_I$ is defined according to the following equations.

$$R_A = 1 - (S_{fr} / S_0)$$  and  $$E_I(\%) = \frac{R_A^{NI} - R_A^{HI}}{R_A^{NI}} \times 100$$  \hspace{1cm} (1)

where $S_{fr}$ is the cross section area of the specimen after rupture, $S_0$ is the initial cross section area of the specimen. $R_A^{NI}$ and $R_A^{HI}$ respectively represent the reduction of area in nitrogen gas and hydrogen blends.

With this definition, $E_I = 0$ means no HE whereas $E_I = 100\%$ is the value for a maximum embrittlement. The indexes in the various hydrogen blends are shown in table 3.

Dealing with the fracture mode, the fractographs were taken by using a scanning electron microscope (SEM) on these smooth specimens, as shown in Figure 3 (In this paper, the fractographs of the specimens
which were tested in nitrogen gas and 20vol% hydrogen blend were taken as representative). The fracture of the specimen tested in nitrogen gas is ductile (Figure 3a). The ductile-dimple as the dominant feature is observed on the fracture surface, as shown in Figure 3b. Figure 3c shows the fractograph of the specimen tested in 20vol% hydrogen blend. The necking is reduced significantly compared to the specimen tested in nitrogen gas. The surface cracks are found on the specimen side surface marked by the red box. The crack initiates from region A near the specimen surface and the occurrence of delamination (secondary cracks) can be found on the fracture surface, it might be related with the textured microstructure caused by hot rolling. A higher-resolution SEM image of region A is shown in Figure 3d.

![Fracture surfaces](image)

**Figure 3.** Fracture surfaces of the smooth specimens tested in nitrogen gas (a and b) and in 20vol% hydrogen blend (c and d).

<table>
<thead>
<tr>
<th>Added hydrogen /vol%</th>
<th>0</th>
<th>5</th>
<th>10</th>
<th>20</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$ /%</td>
<td>0</td>
<td>3.39</td>
<td>4.32</td>
<td>15.88</td>
<td>16.77</td>
</tr>
</tbody>
</table>

### 3.1.2 Notch tensile properties

The influence of hydrogen concentration on the tensile behavior of the notch tensile specimens with a notch root radius of 0.1mm is shown in Figure 4. The notch tensile strength ($\sigma_N$) is defined as the maximum load divided by the initial minimum cross section area, which is calculated as follows:
\[ \sigma_N = \frac{F_{\text{max}}}{S_{\text{min}}} \]  

(2)

where \( F_{\text{max}} \) is the maximum tensile load and \( S_{\text{min}} \) is the initial cross section net area of the notch. In view of the effect of the added hydrogen on the fracture stress, another parameter \( RNS \), the reduction of the notch tensile strength, is also defined to describe the HE susceptibility of the steel which is calculated as follows:

\[ RNS(\%) = \left( 1 - \frac{\sigma_N}{\sigma_{N0}} \right) \times 100 \]  

(3)

where \( \sigma_{N0} \) is the notch tensile strength of the specimen in nitrogen gas.

Compared with the result obtained in nitrogen gas, \( \sigma_N \) decreases with increasing hydrogen. As the result, \( RNS \) increases, which implies that the HE susceptibility of the X80 pipeline steel is proportional to the hydrogen concentration. Besides, the fracture occurs earlier and the reduction of area decreases when more hydrogen is added, the corresponding data is given in Table 4.

![Figure 4. Influence of hydrogen concentration on the tensile properties of the notch tensile specimens](image)

<table>
<thead>
<tr>
<th>Added hydrogen vol%</th>
<th>Notch tensile strength MPa</th>
<th>RNS %</th>
<th>Reduction of area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1271.36</td>
<td>0</td>
<td>37.55</td>
</tr>
<tr>
<td>5</td>
<td>1253.49</td>
<td>1.41</td>
<td>30.41</td>
</tr>
<tr>
<td>10</td>
<td>1222.12</td>
<td>3.87</td>
<td>29.86</td>
</tr>
<tr>
<td>20</td>
<td>1190.25</td>
<td>6.38</td>
<td>22.20</td>
</tr>
<tr>
<td>50</td>
<td>1150.16</td>
<td>9.53</td>
<td>17.07</td>
</tr>
</tbody>
</table>
Figure 5 shows the fractographs of the notch specimens. The cracks initiate in the vicinity of the notch root (Figure 5a) and a shear lip (SL) is observed on the fracture surface in nitrogen (Figure 5b). As like as the description above, the ductile-dimple microscopic plasticity feature dominates the fracture surface (Figure 5c). To the specimen in 20vol% hydrogen blend, as shown in Figure 5d, the crack also initiates in the vicinity of the notch root and in a brittle mode, causing a quasi-cleavage fracture as shown in Figure 5f. No shear lip is found on the fracture surface (Figure 5e). Toward the center of the specimen (region A), a more ductile mode of failure occurs as an exception, which probably occurred once the surface cracks covered a threshold area of the cross section.

Figure 5. Fracture surfaces of the notch specimens in nitrogen gas (a, b and c) and 20 vol% hydrogen
3.2 Crack growth properties

It was proven that a pipeline that has been operated under fluctuating pressures is more sensitive to degradation. Hydrogen degraded the fatigue behavior additionally [12,13]. As observed by several authors [14], there is a strong need to improve the knowledge of the fatigue behavior of the materials in hydrogen containing environment in order to derive the safety guidelines for the design of these pipelines.

Fatigue crack propagation tests have been carried out within this study on the Compact Tensile specimens in accordance with ASTM standard E647. The load frequency is 1Hz and the stress rate is 0.1 with the force range of 19kN. The results are shown in Figure 6. The fatigue crack growth rate increases by at least an order of magnitude in hydrogen blends compared to nitrogen gas. In addition, the fatigue crack growth rate increases slightly with the increasing hydrogen content from 5% to 50%.

![Figure 6. da/dN versus △K curves in nitrogen gas and hydrogen blends.](image)

4.0 DISCUSSION

HE in pipeline steels has been quantified extensively through tensile reduction of area and elongation measurements [11,15,16]. However, most of these tests were performed with the cathodic charging methods, which hardly represent the real service state of steels that suffer from load and environment coupled damage process. Here, we directly study the environmental HE of X80 steels in natural gas/hydrogen mixtures by a testing machine with an autoclave.

Previous studies have found that the effect of hydrogen on the fracture behavior of high strength steels may depend on the specimen types [17]. For the notch tensile specimens under axial loading in hydrogen containing environment, it is evident that hydrogen is easy to accumulate in front of the notch root where stress concentration occurs and causes a cohesive stress decreasing zone in the vicinity of the notch root [18], which may lead to the reduction of fracture strength and promote brittle fracture. When the hydrogen concentration of the high stress zone reaches a critical value through stress assisted diffusion and accumulation, micro-crack initiates and then grows up with the further diffusion of hydrogen. As
shown in Figure 5d, the length along X of the center region A was longer than the length along Y, which implies the crack growth rate of Y orientation is faster, it is likely that the textured microstructure plays an important role in the crack propagation behavior of the notch specimen. Nevertheless, the brittle sign is weak on the fracture surface of the smooth specimen in the same environment (Figure 3c). Thus, we can guess that the influence of the texture is more severe for the notch specimens. Besides, compared with the notch specimens tested in nitrogen gas, there is no shear lip on the fracture surface in 20vol% hydrogen blend, which means that hydrogen induced crack is closer to the notch root. With respect to the shortened fracture time of the notch specimens and the accelerated crack growth rate of Compact Tensile specimens, it likely depends on the dislocation movement assisted hydrogen diffusion.

It also seems clear that the amounts of added hydrogen plays an important role, that is, mixing higher percentages of hydrogen into the natural gas bulk causes higher hydrogen partial pressure, eventually increases the concentration of dissolved hydrogen in X80 steel, which promotes HE. This experimental fact may be explained by using Sievert’s law [20], which predicts the hydrogen solubility proportional to $\sqrt{P_H_2}$.

In a practical application, there are many flaws which come from fabricate and assemble processes on the pipeline. To ensure the safety of the existing natural gas pipeline for transporting natural gas/hydrogen mixtures, it is essential to take into account the notched properties in hydrogen containing environment on account of the safety assessment of pipeline. From the test results of the notch specimens in mixtures, it can be concluded that the HE degree is related to the quality of rolling process and the amounts of added hydrogen. In order to mitigate or avoid the HE of X80 steel, improving the rolling process and choosing a proper volume fraction of hydrogen are of great importance.

5.0 DESIGN CALCULATION

Designed life calculation of high-pressure pipeline can be realized by means of a fracture mechanics based approach as long as the fatigue and fracture toughness data is known. The relationship between the increment of fatigue crack growth per cycle (da/dN) and the stress intensity factor range (ΔK) is generally described by a power law relationship [21]

$$\frac{da}{dN} = C\Delta K^m$$

(4)

in which C and m are crack growth rate factors and they are constants. The values of C and m correspond to the various environment were obtained from the curves in Figure 6, after they were fitted by using the least square method. The results are shown in Table 5.

<table>
<thead>
<tr>
<th>Added hydrogen /vol%</th>
<th>0</th>
<th>5</th>
<th>10</th>
<th>20</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>2.259E-8</td>
<td>2.495E-7</td>
<td>2.877E-7</td>
<td>3.304E-7</td>
<td>4.613E-7</td>
</tr>
<tr>
<td>m</td>
<td>2.59</td>
<td>2.59</td>
<td>2.59</td>
<td>2.59</td>
<td>2.59</td>
</tr>
</tbody>
</table>

The fracture toughness of X80 steel data was not measured in this study. For the nitrogen gas environment, the fracture toughness is assumed to be equal to which is measured in air, its value is
On the other hand, some studies have found that the fracture toughness of C-Mn alloys measured in hydrogen gas is sensitive to gas pressure [23-25], but the recent fracture toughness measurements found that the varying hydrogen pressure from 5.5MPa to 21MPa did not significantly affect fracture toughness for either the X60 steel or the X80 steel [26-27], so a conservative value of 102 MPa m in reference [22] was used for the hydrogen blends.

Following Article KD-10 in the ASME Boiler and Pressure Vessel Code, Section VIII, Division 3, a sample calculation was performed to estimate the effect of hydrogen to the designed life of high-pressure pipeline. The example pipeline is designed to bear a pressure up to 12MPa, which has an outer diameter of 1000mm. The wall thickness (t) of this pipeline is calculated according to the Chinese standard GB 50251 (2003). Here we omit the particular calculation process and the wall thickness is equal to 15 mm. The pipeline is assumed to experience severe operating conditions such that its pressure fluctuates from 1.2MPa to 12MPa three times a month. For the calculation, an initial flaw depth (a0) is set at 0.5mm on the basis of the regulation in Japanese standard KHKS 0220, which depends on t. It is assumed that this flaw would begin propagating in fatigue during the first pressure cycle. The flaw is assumed to have a semi-elliptical shape on the inside surface with a depth (a) to length (2c) ratio, a/2c = 1/3, and is aligned with the longitudinal axis of the cylindrical vessel and propagating radially outward.

The stress intensity factor (Kf) for this flaw is determined from the internal pressure (p), and wall thickness using the following solution for a finite length, part-through thickness flaw [21]

\[
K_f = \left( \frac{p r}{t} \sqrt{\frac{\pi a}{Q}} \right) F
\]

(5)

where

\[
F = 1.12 + 0.055 \xi^2 + \left( 1 + 0.02 \xi + 0.019 \xi^2 \right) \frac{\left( 20 - \frac{t}{r} \right)^2}{1400}
\]

\[
\xi = \frac{2c}{t}
\]

\[
Q = 1 + 1.464 \left( \frac{a}{c} \right)^{1.65}
\]

\[
r = 0.25 (ID + OD)
\]

in which ID and OD represent internal diameter and outer diameter of the pipeline, respectively. The crack is assumed to propagate at a rate measured from the fatigue crack growth experiments (Table 5) such that

\[
a_{i+1} = a_i + \frac{da}{dN} \Delta N
\]

(6)
where
\[
\frac{da}{dN} = C(\Delta K)^n
\]

Crack length is re-calculated for each \(\Delta N=5\) cycles. The crack is assumed to have reached a critical crack depth \((a_c)\) when \(K_{\text{max}}\) is equal to the fracture toughness as mentioned above. The calculated number of design cycles \((N_p)\) is defined as the lesser of the number of cycles corresponding to one-half of the number of cycles required to propagate a crack from the initial assumed flaw depth to the critical crack depth and the number of cycles required to propagate a crack from the initial assumed flaw size to the depth of min \(\{0.25 a_c, 0.25 r\}\), which represents the smaller value of this two.

The results of the sample calculation for \(N_p\) and the fatigue life \((L)\) of the example pipeline which contains various volume fraction of hydrogen are shown in Table 6, assuming that the pipeline pressure fluctuates from 1.2 to 12MPa three times a month, an estimate that considers the effect of the shutdown and failure like leak or burst to fatigue life. It clearly indicates that the added hydrogen decreases the designed life of high-pressure pipeline dramatically compared with the designed life under nitrogen gas, the value of \(L\) is 783 in nitrogen gas versus 68 in 5vol% hydrogen, and it decreases continuously with increasing hydrogen. The service life of the oil and gas pipelines is generally up to 50 years, the sample calculation is limited to the effect of pressure fluctuation on the designed life of pipeline, the corrosion, real defects in material, real gas composition, natural force and other outside force are not taken into account, unluckily, these factors seriously effect life of pipeline, the calculated results are thus larger. With regard to choose a proper volume fraction of hydrogen to blend into natural gas, it is questionable, at least for 20vol% or higher.

<table>
<thead>
<tr>
<th>Added hydrogen /vol%</th>
<th>0</th>
<th>5</th>
<th>10</th>
<th>20</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>(N_p) /cycles</td>
<td>28195</td>
<td>2477</td>
<td>2150</td>
<td>1872</td>
<td>1342</td>
</tr>
<tr>
<td>(L/a)</td>
<td>783</td>
<td>68</td>
<td>59</td>
<td>52</td>
<td>37</td>
</tr>
</tbody>
</table>

### 6.0 CONCLUSION

For the reason that HE of metals may occur when the pipeline steel is subjected to concurrent hydrogen invasion with mechanical loading while being exposed to hydrogen containing environments directly. For safety consideration, it is indispensable to study the effect of added hydrogen produced from renewable energy on pipeline steel in order to achieve a large-scale transportation by existing NG pipeline. In this study, the mechanical properties of X80 pipeline steel were tested in natural gas/hydrogen mixtures with 0, 5.0, 10.0, 20.0 and 50.0vol% hydrogen at the pressure of 12MPa. The conclusions are as follows:

1. The amounts of added hydrogen plays an important role in HE of X80 steel. The parameters \(E_t\) and \(RNS\) respectively corresponding to the smooth and notch specimen increase progressively and the fatigue crack growth is significantly accelerated with increasing hydrogen.

2. The fractographs of the tensile specimens show the brittle fracture characteristic of quasi-cleavage in
hydrogen blends compared to the ductile characteristic of dimples in nitrogen gas. Nevertheless, the brittle sign is weak on the fracture surface of the smooth specimen in the same environment.

(3) The textured microstructure caused by hot rolling has effects on HE, and the notch specimens seem to be more affected by the texture.

(4) The designed life of the X80 steel pipeline is degraded by the added hydrogen dramatically, which is 783 years in nitrogen gas versus 68 years in 5vol% hydrogen, and it decreases continuously with increasing hydrogen.

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REFERENCES


