Abstract

This paper provides an overview of detection, assessment and evaluation methods of hydrogen attack in steels. Equipment in contact with H₂ at high temperature and pressure may suffer from hydrogen damage - Hot Hydrogen Attack. Atomic hydrogen diffuses readily in steels and cracking may result from the formation of CH₄ or H₂ at high pressure and temperature in internal voids in the metal. This results in fissuring at grain boundaries and decarburisation with loss of strength, which makes the material unreliable or dangerous.

It has been shown that the sound attenuation in hydrogen-damaged steel can be used to quantify the level of degradation of the material's mechanical properties. Knowing this, the remaining life of an affected plant can be estimated.

Keywords: Assessment, Examination, Failure, Hydrogen attack, Hydrogen damage, Life estimation.

1. INTRODUCTION

Hydrogen has a diverse range of harmful effects on metals. Hydrogen induced degradation of metals is caused by exposure to atmosphere, where hydrogen is absorbed into the material and results in reduction of its mechanical performance. The severity and mode of the hydrogen damage depends on:

- source of hydrogen - external (gaseous)/internal (dissolved),
- time of exposure,
- temperature and pressure,
- presence of solutions or solvents that may undergo some reaction with metals (e.g. acidic solutions),
- type of alloy and its production method,
- amount of discontinuities in the metal,
- treatment of exposed surfaces (barrier layers, e.g. oxide layers as hydrogen permeation barriers on metals),
- final treatment of the metal surface (e.g. galvanic nickel plating),
- method of heat treatment,
- level of residual and applied stresses.

Depending on the combination and number of the above variables, the hydrogen damage may be classified as shown below:

- Hydrogen Embrittlement,
- Hydride Embrittlement,
- Solid Solution Hardening,
- Creation of Internal Defects,

and can further be subdivided into various damaging processes as shown in Figure 1.

![Figure 1: Classification of hydrogen damage](1)

### 1.1 Hydrogen Attack Mechanism and Prevention

As it was said in the previous section, hydrogen forms methane bubbles within the material while reacting with the carbon of the steel. The methane bubbles form on the grain boundaries and in minute voids. Methane pressure build-up due to expansion and joining of such bubbles extends the voids into fissures. The growth of fissures and voids weakens the metal and the fissures develop into major cracks.

The degree of hydrogen attack depends on temperature, hydrogen partial pressure, stress level, exposure time, steel composition and structure.

Hydrogen attack has been reported in plain carbon steel, low alloy steels and even some stainless steels operating above 473K. [1][2]

Hydrogen attack is one of the major problems in refineries, where hydrogen and hydrocarbon streams are handled up to 20 MPa and approximately 810K level. [2]

In order to prevent hydrogen attack from occurring at high temperature and/or pressure, a high alloy element content is required. Chromium (Cr), molybdenum (Mo), Tungsten (W), Vanadium (V), Titanium (Ti), Niobium (Nb) - carbide forming elements - are used in steel to provide desired resistance.

API 941’s Nelson Curves, based on industry experience provide guidance universally used for alloy selection. The appropriate alloy to select is shown as the curve immediately to the right or above the temperature-hydrogen partial pressure coordinates, which represent anticipated parameters of operation.

Heat treatment influences steel resistance to hydrogen attack.

For example, quenched and tempered 2-1/4Cr - 1Mo steel has increased susceptibility to hydrogen cracking due to low resistance of martensitic and bainitic structures to hydrogen damage.

The heat treatments that would produce excessive yield strength levels should be avoided or used with caution.
Industry experience indicates that post-weld heat treatment of Cr-Mo steel is beneficial in resisting hydrogen attack in hydrogen service.

It is a common practice to require a manufacturer of a hydrogen-hydrocarbon equipment to run embrittlement tests on weld consumables and store all "low hydrogen" electrodes in hot 'boxes'; before fabrication is begun. Preheat requirement on low chromium steel results in minimizing weld cracking caused by hydrogen during fabrication.

Proper inspection, quality control, good design and a reputable manufacturer are all necessary to assure a finished vessel or reactor will be resistant to hydrogen attack.

2. DETECTION AND QUANTIFICATION OF HYDROGEN DAMAGE

Unsatisfactory service experience with the Carbon - 1/2Mo steel had led to reconsideration of the curves originally provided by API 941. Currently API 941 warns against new construction with the alloy and urges inspection and monitoring of existing equipment.

There are a number of inspection methods available. Most of them are based on ultrasonics.

1. Ultrasonic Echo Attenuation Method,
2. Amplitude-based backscatter,
3. Velocity ratio,
4. Creeping waves/Time-of-Flight Measurement,
5. Pitch-catch mode shear wave velocity
6. Ultrasonic method based on backscatter and velocity ratio measurement,
7. AUBT - Advanced Ultrasonic Backscatter Techniques,
8. Method based on TOFD, Thickness mapping, backscatter and velocity ratio,
9. In-situ Metallography - replicas.

The overview of these techniques is given in the table below:

<table>
<thead>
<tr>
<th>Inspection Method</th>
<th>Equipment Required</th>
<th>Principle</th>
<th>Advantages</th>
<th>Limitations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultrasonic Echo Attenuation method</td>
<td>Ultrasonic flaw detector or pulser/receiver and oscilloscope, longitudinal wave transducer.</td>
<td>This technique measures the loss of back-wall echo amplitudes as an indication of hydrogen damage.</td>
<td>Low cost, Simple to use.</td>
<td>It has no ability to discriminate hydrogen attack from abnormal grain size, inclusions, laminar cracks, rough surfaces, internal surface geometry, cladding, disbondment between cladding and base metal. Not recommended as a stand-alone method for detection of hydrogen attack.</td>
</tr>
<tr>
<td>Amplitude-based backscatter</td>
<td>Ultrasonic flaw detector or pulser/receiver and oscilloscope, longitudinal wave</td>
<td>This technique measures the amplitude of backscattering signals and uses high backscattering amplitude as the indication of hydrogen damage.</td>
<td>Low cost, Simple to use.</td>
<td>It cannot differentiate hydrogen attack from internal flaws such as laminar cracks and inclusions. The validity of the technique also depends on the surface condition of the</td>
</tr>
<tr>
<td>Method Type</td>
<td>Equipment Required</td>
<td>How the Technique Measures Hydrogen Attack</td>
<td>Complexity</td>
<td>Cost</td>
</tr>
<tr>
<td>-------------------------------------</td>
<td>-------------------------------------------------------------------------------------</td>
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<tr>
<td>Velocity ratio</td>
<td>Ultrasonic flaw detector or pulser/receiver and oscilloscope, longitudinal and shear wave transducers</td>
<td>This technique measures the shear-to-longitudinal wave velocity ratio of the entire wall thickness to assess the extent of hydrogen damage.</td>
<td>Relatively simple to use. Low cost.</td>
<td>Cladding materials influence the results. It cannot identify hydrogen damage less than 15% of the wall thickness.</td>
</tr>
<tr>
<td>Creeping waves/Time-of-Flight measure-ment</td>
<td>Ultrasonic flaw detector or pulser/receiver and oscilloscope, creeping wave transducer</td>
<td>This technique measures the reduction of creeping wave velocity as the indication of hydrogen damage.</td>
<td>Relatively simple to use. Low cost.</td>
<td>It is applicable only to partially damaged steel and only to thin-walled vessels.</td>
</tr>
<tr>
<td>Pitch-catch mode shear wave velocity</td>
<td>Ultrasonic flaw detector or pulser/receiver and oscilloscope, set of shear wave transducers</td>
<td>The relative change in shear wave velocity is measured and correlated to the extent of hydrogen damage,</td>
<td>Relatively simple to use. Low cost.</td>
<td>The technique cannot differentiate hydrogen attack from change of material thickness. Its sensitivity to hydrogen damage is low.</td>
</tr>
<tr>
<td>Ultrasonic method based on backscatter and velocity ratio measurement</td>
<td>Ultrasonic flaw detector and pulser/receiver and oscilloscope, set of shear and longitudinal wave transducers</td>
<td>To detect suspect areas (areas affected by hydrogen attack) the backscatter technique is used. To confirm the findings of the backscattering measurement, the sound velocity measurement method is employed.</td>
<td>Relatively simple to use and accurate method.</td>
<td>Cannot be used to its full extent on clad and complicated geometry areas (see velocity ratio and scatter method limitations)</td>
</tr>
<tr>
<td>AUBT - Advanced Ultrasonic Backscatter</td>
<td>Ultrasonic flaw detector and pulser/receiver</td>
<td>A pattern-based backscattering technique is used as the initial screening method. Depending on the</td>
<td>Determines the distance of hydrogen attack</td>
<td>Requires some degree of skill in interpreting pulse-echo patterns.</td>
</tr>
</tbody>
</table>

transducer. calibration material, the material under examination as well as on the pressure applied on the ultrasonic transducer.
<table>
<thead>
<tr>
<th>Techniques</th>
<th>Pulse-echo backscatter pattern observed, one of several follow-up techniques, including frequency dependent backscatter, direction dependent backscatter, velocity ratio, spectral analysis and spatial averaging can be used to determine the cause of backscattering signal.</th>
<th>Progression. Can be used to determine the material mechanical properties of the hydrogen-damaged region.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Method based on TOFD, thickness mapping, backscatter and velocity ratio</td>
<td>TOFD equipment, thickness-mapping equipment. The backscatter technique is used as an initial scanning then velocity technique and thickness mapping techniques are used to confirm and provide picture of the extent of the damage.</td>
<td>Requires high degree of skill in interpreting TOFD and pulse-echo patterns. Recommended method for detection of hydrogen attack.</td>
</tr>
<tr>
<td>In-situ Metallography - replicas</td>
<td>Grinding discs, abrasive papers. Final cleaning chemicals and polishing suspensions. Acetate films, microscope. Detects microstructure changes in tested areas, degradation of material, micro cracking and their causes (e.g. creep, hydrogen damage). Can be carried out in situ. Gives permanent high-resolution record. Relatively fast and cost effective.</td>
<td>Requires high degree of skill in preparing and interpreting microstructure images. Sensitive to surface contamination. This technique samples small areas only and is not able to measure the depth of the damage. Recently, the replication microscopy technique has become an important NDE method for oil and power industry. Recommended method.</td>
</tr>
</tbody>
</table>

Table 1: Reference Guide to Major Methods of Hydrogen Attack Detection.

2.1 AUBT Advanced Ultrasonic Backscatter Techniques [8]
This technique combines nearly all the mentioned methods into one testing procedure. This procedure can be used as a starting point for prediction of the remaining life of a vessel or reactor from the hydrogen damage point of view. Let us go through the main points of this procedure:

1. An initial scanning procedure for locating areas suspected of being damaged by hot hydrogen attack - a pattern-based backscattering test. The test provides a pattern which is classified as falling within at least one of four backscattering patterns category types, type I, type II, type III and type IV - refer to Figure 2:

Type I backscattering pattern indicates that the internal defect may be through-wall or nearly through-wall.

Type II backscattering pattern is characteristic to a laminar type of defect instead of hydrogen damage.

Type III backscattering pattern - high amplitude signal is at a distance from the backscatter patterns. [8].
back-wall echo or the interface signal of the clad equipment. Type III pattern indicates the internal defect, which may be growing stage of hydrogen damage.

Type IV backscattering pattern indicates that the internal defect may be an initial or growing stage of hydrogen attack.

2. The second step, so called follow-up test, is carried out for each type of backscattering pattern identified for each location.

For the type I pattern in sequential order the following tests are performed:

- Velocity ratio,
- Spectrum analysis,
- Spatial averaging.

For the type II pattern the tests are:

- Frequency dependent backscatter test,
- Spectrum analysis,
- Velocity ratio,
- Spatial averaging.

Type III pattern calls for:

- Frequency dependent backscatter test,
- Spectrum analysis,
- Velocity ratio

The follow-up tests for type IV pattern are:

- Spectrum analysis,
- Velocity ratio,

3. This step recognises the type of the damage in areas where the previous step shows positive identification of hydrogen attack. The damage interpretations are as follows:

- Type I pattern + positive identification of hydrogen damage \(\Rightarrow\) it is the through-wall or nearly through-wall hydrogen damage.
- Type II pattern + positive identification of hydrogen damage \(\Rightarrow\) indicates that the internal defect is the through-wall or nearly through-wall hydrogen damage instead of the defect being a laminar type of discontinuity.
- Type III pattern + positive identification of hydrogen damage \(\Rightarrow\) it is may be either growing type of hydrogen attack or an internal cracking.
- Type IV pattern + positive identification of hydrogen damage \(\Rightarrow\) it indicates the growing stage or initial stage of hydrogen attack.

4. In this step the distance of the hydrogen attack is determined.

The equation shown below describes the distribution of backscattering amplitude in the through-wall direction in hydrogen-damaged materials.
\[ A_x(x) = A_0 T \sqrt{2D(\alpha_0 + \alpha_{HA}(x))} \Delta x * e^{-2 \int_0^x (\alpha_0 + \alpha_{HA}(x')) dx'} \]

where: \( A_x(x) \) = Amplitude of backscattering
\( A_0 \) = amplitude of the incident sound wave
\( T \) = coefficient of sound energy transmitting through the interface between the transducer and the material
\( D \) = fraction of scattering sound energy going in the direction back to the transducer
\( \alpha_0 \) = attenuation coefficient related to material intrinsic properties
\( \alpha_{HA} \) = coefficient of the hydrogen-attack-induced attenuation
\( x \) = distance from the sound entry surface
\( \Delta x \) = pulse length

**Figure 3** shows an example of results calculated from the above equation in comparison with experimental data. The measurement was done on a hydrogen-damaged sample from the non-damaged side with a 10 MHz longitudinal wave transducer, \( \alpha_0 = 0.005 \) and \( \alpha_{HA}(x) \) as shown in **Figure 4**. The increase and then drop in backscattering amplitude is evident. This is a typical image of a backscattering signal.

The distance of possible damage is determined by measuring the time of flight between the front of the backscattering signal and the first peak of the interface signal or the back-wall echo.
5. This step determines the mechanical properties of the damaged area.

Correlations between the mechanical properties of steel and the sound attenuation in the material can be derived from experimental data.

Both attenuation and velocity ratio can be used to quantify the mechanical properties of damaged materials.

Figure 5 shows elongation plotted against velocity ratio. The data were measured using hydrogen damaged carbon-1/2Mo steel samples.

Fig 5: Relation between elongation and velocity ratio [8].

Although both velocity ratio and attenuation can be used to assess mechanical properties, they do not have the same sensitivity. Figure 6 shows the relation between these parameters at 8 MHz. While the attenuation has increased 3 db/in, the velocity ratio stays practically the same, below 0.55. The relation suggests that to assess mechanical properties of damaged materials, the sound attenuation should be used.

It has to be noted that a full set of reference blocks, made of identical or similar material should be available to allow such an evaluation.
In accordance with research results shown in [3] ("Non-destructive Evaluation of Remaining life of Hydrogen attacked 1/2 Mo Steel for Long Term Used Chemical Plants"), reduction of the impact value against the sound attenuation should be pronounced - refer to Figure 7.

3. ESTIMATION OR REMAINING LIFE OF A HYDROGEN-DAMAGED PLANT

The remaining life of a hydrogen-damaged plant can be estimated by use of relation between the level of material damage and mechanical properties and between the material deterioration and hydrogen exposure time.

For a hydrogen-damaged material remaining life can be assessed from the following equation [3]:

\[ t = CP^n e^{(Q/RT)} \]

where:  
\( t \) = remaining life  
\( P \) = hydrogen partial pressure  
\( Q \) = activation energy  
\( T \) = absolute temperature  
\( R \) = gas constant  
\( C, n \) = constants

The chart shown in Figure 7 was produced by evaluating the mechanical properties of carbon-1/2Mo steel exposed to hydrogen environment (up to 11 000 hrs) at partial pressure of 6.9 MPa and temperature 773K, and 9.8 MPa with temperature of 723K. Tensile tests and Charpy impact tests were conducted on the hydrogen exposed specimens.

If the life of hydrogen-attacked material is defined as a reduction of impact energy values to 50% of the original value, the above equation can be rewritten as [3]:

\[ t = 3.92 \times 10^{-5} P^{-5.312} e^{(1.89\times10^5 / 8.31T)} \]

where:  
\( P \) = hydrogen partial pressure (MPa)
T = absolute temperature (K)
\( t = \text{estimated time (hrs)} \)

4. CONCLUSIONS

1. Hydrogen attack is caused by exposure of steel to a hydrogen environment. The severity of the damage depends on the time of exposure, temperature, hydrogen partial pressure, stress level, steel composition and structure.
2. To avoid/prevent hydrogen attack, steels with elements forming stable carbides should be used. A heat treatment should be carefully applied to avoid producing structures with low resistance to hydrogen attack (martensite, bainite). Proper inspection and quality control systems are necessary during the manufacturing process of hydrogen and hydrocarbon handling equipment.
3. Hydrogen undamaged and damaged samples of steel used in plant equipment should be available for the hydrogen attack testing purposes.
4. Recommended methods for detection of hydrogen damage are AUBT - Advanced Ultrasonic Backscatter Techniques, methods based on TOFD, thickness mapping, backscatter and velocity ratio and in-situ metallography - replicas. Results of methods like AUBT can be used for estimation of life of hydrogen attacked equipment.
5. Non-destructive methods based on ultrasonics are able to quantify the hydrogen attack and estimate mechanical properties of hydrogen-damaged steels. The results of such tests can be used in life assessment calculations.

5. REFERENCES

6. Intico Reports.