Low Temperature Hydrogen Damage Assessment in the Gas and Refining Industries

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INTRODUCTION

Hydrogen damage is a degradation mechanism active in the oil and gas industry. The hydrogen atom is the smallest of all atoms and hydrogen attack is similarly insidious and hidden from simple inspection techniques. Hydrogen damage takes place at two temperature regions, elevated temperatures and temperatures at ambient and slightly above. This paper deals with the latter class and will review modern inspection techniques aimed at identifying, quantifying and tracking this form of damage.

DAMAGE CHARACTERISTICS

Ambient hydrogen damage, also referred to as wet H$_2$S damage, can be classified in terms of a number of distinct classes. In all of the classes however, the common factor is that the presence of moisture and H$_2$S is required for the attack:

- Hydrogen Blistering
- Hydrogen induced cracking (HIC)
- Stress Oriented HIC (SOHIC)
- Sulphide stress corrosion cracking (SSC)

![Figure 1 Graphical representation of HIC](image-url)
In all of these mechanisms, the first step in the attack is the formation of free hydrogen atoms at the steel surface. The hydrogen atoms develop from the sulphide attack of the process medium at the steel surface. As a result of the electrochemical reaction, which results when the steel surface is corroded, hydrogen atoms are generated. The hydrogen atoms, being much smaller than the iron crystal lattice, readily diffuse into the steel, even at relatively low temperatures.

The diffusing hydrogen can cause damage to the steel lattice in a number of different ways, and each of these distinct mechanisms leads to a different class of wet H$_2$S damage.

In the case of hydrogen blistering, the hydrogen atoms combine in the lattice to form hydrogen in the molecular form. Due to the fact that molecular hydrogen is much more voluminous than atomic hydrogen, the reaction is accompanied by the formation of significant internal stresses. In certain cases, the internal stresses are high enough to lead to the formation of internal cracks, parallel to the external surface, and blistering occurs (see Fig. 2). The blister, if large enough, can result in bulging of the steel surface, and this is one hydrogen damage mechanism which is can be identified through visual inspection. The blister is normally in the same plane as that of the principal stresses for vessels and piping, and is mostly treated less conservatively than crack-like flaws in Fitness-for-Service (FFS) Assessments.

In the case of Hydrogen Induced Cracking (HIC), smaller blisters form at planes parallel to the surface (See figure 4). Sometimes, neighbouring blisters lying on adjacent planes develop cracks that link the blisters. A step-wise morphology is obtained, hence the name of step-wise cracking, which is sometimes given to HIC. (Fig.5 a & b). The step-wise cracks are sometimes oriented at right angles to the principal stresses for vessels and piping, and are treated conservatively in Fitness-for-Service (FFS) Assessments.
Fig. 5 a and b. Internal hydrogen blister parallel to the internal surface join up as a result of step-wise cracking to form the typical crack profile of Hydrogen-Induced Cracking (HIC) (Fig. 5 a at low magnification, Fig. 5 b enlarged) (example from API RP 571, Dec 2003)

**Sulphide Stress Cracking** (SSC) is a class of hydrogen damage that typically develops in hard spots of welds. It is a result of the effect of the hydrogen (released during the Sulphide corrosion) in assisting crack formation of susceptible (hard) areas in a stress field (Fig. 6). In this case, atomic hydrogen serves to further embrittle the relatively brittle hard regions. The high levels of residual stress present in the welds act as the driving force for the cracking. Cracking occurs in the weld metal itself. These cracks are located in a brittle region and are therefore treated very conservatively in FFS assessments.

Fig. 6. Sketch depicting the typical preferential location of Sulphide Stress Cracking (SSC) in the weld metal (from API RP 571, Dec 2003)
Stress-Oriented Hydrogen-Induced Cracking (SOHIC) often develops from HIC or SSC cracks close to the surface and then grow in a through-wall plane. The cracks are driven by the residual stresses adjacent to the weld in the HAZ and are oriented parallel to a weld (Fig. 7). The cracks are located in highly stressed regions and are treated very conservatively in FFS assessments.

**THE INFLUENCE OF PROCESS VARIABLES**

Process variables exert a strong influence on the occurrence of wet hydrogen damage. Knowledge of these influences can assist in the planning of a survey where greater inspection effort will be concentrated on areas likely to be susceptible to attack.

**Acidity**

Generally, wet hydrogen attack does not occur in neutral environments (pH ~ 7.0). Acidic environments are preferred and a common region for this damage is at pH levels below 4.0 with H$_2$S present. If both H$_2$S and cyanide are present, this form of damage can occur if the pH is basic, at pH levels above values of 7.6.

**H$_2$S concentration**

H$_2$S levels above 50 ppm are normally required for attack. In the presence of cyanides, however, the H$_2$S threshold level for attack reduces remarkably.

**Temperature**

Most of the wet-Hydrogen attack classes occur at operational temperatures between ambient and 150 °C. The exception is in the class of Sulphide Stress Cracking (SSC) which may develop at temperatures between ambient and 80 °C. At elevated temperatures, other forms of hydrogen attack takes place, where that does not require moisture to develop. In these cases, pressure, temperature and partial hydrogen pressure determine if attack can take place.
place and the nature of the damage takes other forms. This type of damage, termed high-temperature hydrogen attack, is beyond the scope of this document.

SURVEYS TO IDENTIFY AND QUANTIFY DAMAGE

In order to assess the level and extent of damage on operational plant, extensive portions of plant often require assessment. A risk-based approach is normally used to prioritise equipment where high probability and consequence of attack is indicated. Areas prone to attack can be identified by a review of the process history, geometry, and operating conditions. The appropriate selection of NDT techniques is important in ensuring that plant availability is optimised and defect detection is maximised.

The ideal situation is to carry out the inspection non-intrusively without having to shut down the operating plant. In order to achieve this a combination of 0° compression wave, Time of Flight Diffraction (ToFD) and 45° shear wave ultrasonic inspection techniques are used.

DETECTION AND MONITORING

The inspection process is divided into 3 specific steps intended to detect any evidence of Low Temperature Hydrogen Attack initially using a cost effective and reliable manual ultrasonic procedure with automated and semi automated techniques subsequently employed to image, record and size any damage. The resultant data can then form the basis of a propagation monitoring programme to allow plant operators to plan any interventions that may be required during plant shutdowns.

Level 1 Ultrasonic Inspection:

- ToFD of longitudinal and circumferential welds
- Manual 0° pulse echo of shell and dished end material
- Manual shear wave inspection of nozzle welds

Level 2 Ultrasonic Inspection:

- Colour graphic imaging of selected areas – medium resolution scan

Levels 3 and 4 Ultrasonic Inspection:

- Colour graphic Imaging of selected areas – high resolution scan
- ToFD and 45° shear wave slicing
- Typical Scanner set up as illustrated in figure 9

Figure 9 Dual axis scanner used for level 3 and 4
Level 1 Ultrasonic Inspection:

The level 1 manual pulse echo technique is used as the initial screening technique with all indications recorded and displayed as indicated on figure 10. The data is reviewed and areas showing evidence of suspected hydrogen damage are selected for further inspection at level 2. Areas or items of plant equipment showing no evidence of hydrogen damage at the level 1 inspection stage are not subjected to any further inspection.

Level 2 Ultrasonic Inspection:

The primary purpose of the level 2 scan is to define the full extent of possible hydrogen damage of the area of the item being inspected. At this stage the through wall extent of the indications is not known nor is any disposition as to the exact nature of the damage made. The results of the level 2 inspection is recorded and displayed per figure 11.
Levels 3 and 4 Ultrasonic Inspection:

The level 3 inspection consists of high resolution 0° colour graphic imaging of selected areas in order to provide detailed information on the type of hydrogen damage and to assist in dipositioning the damage. Collected data is as displayed in Figure 12b.

The Level 4 inspection consists of ToFD and 45° shear wave slicing over all areas inspected at level 3. The information gained from these levels of inspection provides an exact statement of through wall extent of the indications as well as providing definitive information on the presence on any inter-ligament cracking or connection to the process surface.

Figure 12 a Graphical display of probe deployment and Figure 12 b high resolution “C” Scan Image of HIC

Figure 13 “D” Scan ToFD Images of HIC
It is clear that only after all the stages of the inspection have been completed can a statement be made as to the extent and disposition of indications as well as to the presence of inter-ligament cracking and the through wall extent of indication detected.

ASSESSMENT OF FLAWS

In the case of the detection of flaws, decisions have to be made in terms of the acceptability thereof. In this regards, documents such as API RP 579 of 2000 provide guidance and internationally accepted best practices.

Damage Classification

Accordingly, the classification of the damage type is the first and critical step. For example, a step wise cracking flaw of the same dimensions and location as that of a hydrogen blister will be assessed as being much more critical than the blister. In practical terms, it may be difficult to ascertain if step-wise cracking has initiated from blisters, making the distinction between blisters and HIC difficult. If any possibility exists that cracking may have initiated, one has to act conservatively and assume that the flaw does represent HIC rather than just blistering. In this regard, ToFD and 45° slicing has proved to be very valuable.

Flaw Sizing

The accurate sizing of a flaw follows the characterisation of the flaw type. In order to assess the flaw, one has to establish the flaw dimensions along three reference axes. The shortest distance from the closest surface to the flaw is also required, as is the location of the closest discontinuities (flanges and internals, for example) as well as that of other flaws. Advanced NDT techniques such as TOFD and 45° slicing are necessary to provide answers to these questions. This information also needs to be recorded and presented in such a manner as to provide all the details that would be essential to carry out the Fitness for Service assessment. One of the ways of doing this is to record the indications on an indication assessment sheet, which collates the information as to the location of the indication as well as defect type and dimensions. An example is provided in Figure 15.
For some assessments, knowledge of the current steel properties may be required. In hydrogen service, and in the case of confirmed hydrogen attack, hydrogen atoms have diffused into the steel and, if present, can result in a marked decrease of the fracture toughness. The fracture toughness reduction can however not be assessed using standard techniques such as Charpy V-Notch testing, for example. If the establishment of fracture toughness properties is required for the flaw assessment, as is in the case for crack-like flaws, a worst case approach, assuming hydrogen saturation, is normally followed in assessment. This approach is detailed in API RP 579 Appendix F, and it establishes the crack-arrest fracture toughness of the steel from the original design information or from original materials testing certificates. The approach indicates the lower-bound fracture toughness as a function of temperature and can be used with confidence as a conservative approach.

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Figure 15 Indication Assessment Sheet

Materials properties

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