

Diffusible Hydrogen in Steel Weldments

- A Status Review[†]

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Abstract

Despite being a subject of intense research and exclusive attention over the past several decades, hydrogen in the weldments of high strength steels continues to seriously limit the performance of the components and confounds the quantitative component prognosis. More than 1500 studies in the literature have reported the behavior and effects of hydrogen in steels and their welds. It is well documented that a sufficient amount of hydrogen, when combined with a crack susceptible microstructure and the weld residual stress, poses a greater risk of hydrogen assisted cracking (HAC). Cracking is undesirable in a weld because it causes a reduction in the mechanical properties, and thus poses a potential threat towards the structural integrity of the weldment. Of particular concern are the facts that HAC occurs at ambient temperatures, appears hours or days after the completion of welding and the cracks often remains undetected. Therefore, HAC may also cause catastrophic failure of a weld component while in service. It is known that the risk of cracking in welds can be reduced either by eliminating or by lowering at least one of the three following factors, the weld hydrogen content, the residual tensile stress and the crack susceptible microstructure of the weld, to levels below the critical to cause HAC. Reduction of hydrogen content in the weld is considered as the best way of reducing the risk of HAC. This can be achieved by employing dehydrogenation heat treatments to the steel and the weld. To choose a suitable dehydrogenation temperature, a knowledge of the hydrogen content in the weld is essential. Hydrogen in the steel weldments exists as diffusible and residual hydrogen. At a given temperature, while the residual hydrogen is permanently trapped in the weld and plays no role in HAC, the diffusible hydrogen is able to diffuse within or out of the weldment and is responsible for HAC. This brings out to the fore the need for the determination of diffusible hydrogen content in a weld. However, hydrogen is a transient element in steel and does not await its measurement like other elements. Therefore, development of a standard specimen and a standard procedure for the measurement of diffusible hydrogen is a daunting task. However, during the past few decades, several methods have been developed, tested and standardized for this purpose. This paper presents an overview of different aspects of hydrogen in steel welds and a systematic review of the different methods developed over the years for diffusible hydrogen measurement in steel welds.

KEY WORDS: (Hydrogen assisted cracking), (Diffusible hydrogen), (Standard method), (Mercury method), (Hot extraction), (Gas chromatography), (PEMHS)

1. Introduction

The damaging effects of hydrogen in steel, generally known as hydrogen embrittlement, have long been recognized [1]. Hydrogen embrittlement in steel is well documented as an issue of contention towards the structural integrity of steels [2]. One of the severe manifestations of the hydrogen embrittlement is hydrogen assisted cracking (HAC) in steel weldments. HAC has received considerable attention in the literature owing to its prevalence in steel welds [3]. Regardless of the extensive research and developments, HAC is still experienced regularly by fabricators, particularly during the welding of high-strength structural steels [4, 5]. HAC is not just confined to welding. It can also occur in the steels during manufacture, during fabrication and in

service. Therefore, heavy responsibilities are placed on the fabricator to employ appropriate safeguards in the welding procedures to prevent HAC. In this regard, the fabricators aim to control either hydrogen content or the hardness of steel depending upon the steel composition. The hydrogen control approach is applied to the high strength steels. In this approach, the fabricators generally rely on preheating, interpass temperature control, post heating and post weld heat treatment, combined with the use of low-hydrogen basic-type welding consumables to reduce the risk of HAC. In this process, the choice of a safe preheat temperature requires a knowledge of the hydrogen content in a weldment which provides a starting point to reduce the risk of HAC [6]. The knowledge of hydrogen content also helps in classifying the welding

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consumables based on their hydrogen contents. This paper presents a brief overview of HAC and different other aspects of hydrogen in steel weldments and a review of various methods for the measurement of hydrogen in weldments.

2. HAC in steel weldments

2.1 Causes, Consequences

Hydrogen assisted cracking (HAC), also known as cold cracking or delayed cracking or underbead cracking, is one of the most prevalent problems encountered in the welding of ferritic steels. HAC is known to markedly lower the mechanical properties such as ductility, fracture strength and fracture toughness of a weldment [7]. There are two deteriorating concerns associated with the occurrence of HAC. First, the probability of HAC in a weld joint is maximum at temperatures in the range of -50 to 150°C, which also covers the ambient temperatures [8]. Second, HAC of a weld joint is often delayed for hours or even days after the welding and although extensive, the cracks may be difficult to detect. Therefore HAC poses the danger of causing catastrophic failure of the weld joint while in service. Intense research has been carried out to understand the role of hydrogen in HAC and to develop standard practices to reduce the risk of cracking. As a result, the role of hydrogen in the formation of cold cracks in the weld joints is established to a major extent if not as a whole. It is widely accepted that HAC is a phenomenon in which hydrogen in a weld joint causes cracking of the joint in the presence of a crack susceptible hard microstructure and tensile residual stress in the weld joint. The three above conditions causing HAC are illustrated in **Fig. 1**. With the presence of hard microstructures in the weld metal or in the heat-affected zone, the susceptibility to HAC increases with the increasing levels of hydrogen and high tensile residual stresses during the cooling. Cracking becomes more prevalent as the temperature approaches room temperature. As shown in **Fig. 2**, this can be attributed to the increase in stress and the local hydrogen content with the decrease in the temperature during cooling. The three conditions necessary to cause HAC in a weldment are discussed below.

2.1.1 Sufficient amount of hydrogen:

Arc welding processes are frequently used in the welding of high strength steels (carbon and low alloy steels). During the welding, the arc temperature is very high; typically around 10,000°C [9]. Such high temperatures produce an arc plasma by dissociating almost all the molecules present in the arc column to ions. In the processes, such as the shielded metal arc welding (SMAW), submerged arc welding (SAW) and flux cored arc welding (FCAW), a flux is used in the welding consumables to prevent the molten metal from oxidation during welding. The flux has several ingredients having chemically bonded water (H_2O) in their structure. The chemically bonded water is dissociated in the welding arc to produce hydrogen. Therefore, hydrogen is introduced

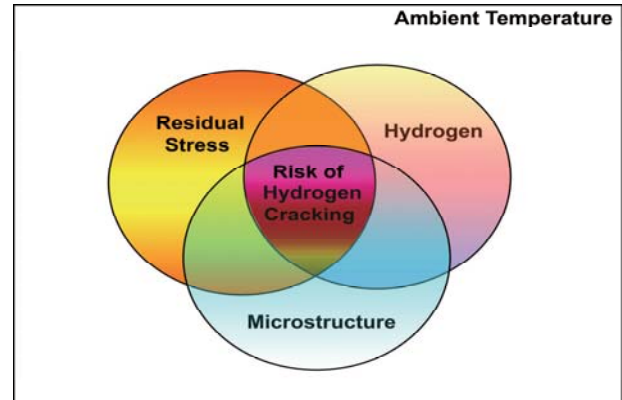


Fig. 1 An illustration of the three essential conditions occurring simultaneously to cause HAC

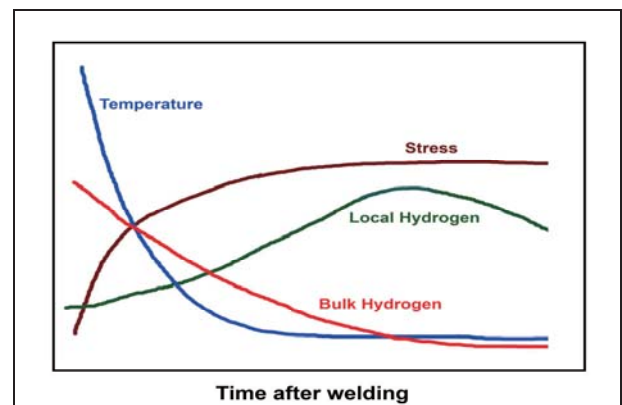


Fig. 2 Variations in the bulk, local hydrogen content and stress during cooling [5]

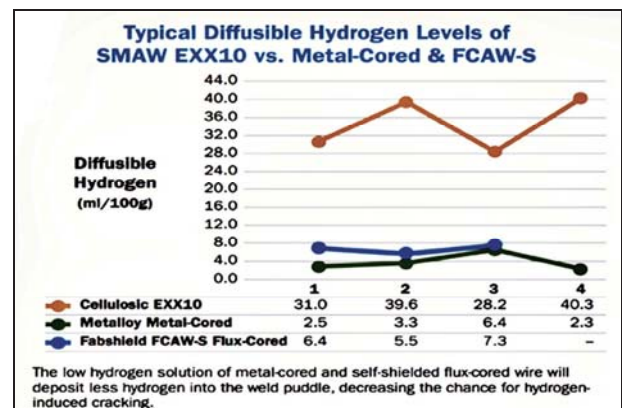


Fig. 3 Hydrogen introduced in different welding processes

to some extent into the weld pool in all the flux bearing welding processes [10, 11]. **Figure 3** shows the different amounts of diffusible hydrogen introduced in different welding processes. Generally, hydrogen content of the weld metal in SMAW is higher than that in the FCAW and SAW processes.

As the solubility of hydrogen in steel increases at higher temperatures, a large amount of hydrogen is dissolved in the molten weld metal. However, the solubility is reduced significantly during the cooling of

the molten weld metal. Also, since the cooling is fast, the dissolved hydrogen can not find sufficient time to diffuse out of the solidifying weld metal. Therefore, the weld metal becomes supersaturated with hydrogen at the end of welding. The supersaturated hydrogen has a propensity to diffuse within or out of the weldment. A portion of hydrogen may also remain trapped in the weldment.

2.1.2 Tensile residual stress in the weldment:

During the welding, the application of heat is highly localized. The localized heating and the rapid cooling of the weldment causes thermal expansion and contraction which results in the tensile residual stress in the weldment. The stress is concentrated at the root and the toe of the weld and also at the notches formed by inclusions and other defects. The local stress may be complemented by any external stress applied immediately after the welding [5]. The stress developed in a weld depends upon the size and geometry of the weld, yield strengths of the weld metal and the parent metal and the external restraint. Also, it is known that HAC increases with decreasing strain rate [12]. Since the strain rate is lowered during the final stages of cooling [13, 14], the susceptibility to HAC is higher at the final stages of cooling.

2.1.3 Susceptible microstructure:

For both the C-Mn and the low alloy steels, the harder the microstructure, the greater is the risk of HAC. The microstructure produced in a welded component depends upon the cooling rate, the composition and hardenability of the parent metal and the weld metal and the prior austenite grain size before transformation. During welding, the heat affected zone (HAZ) closest to the fusion boundary experiences peak temperatures and may transform into austenite. The austenite may be transformed into hard martensite or bainite as a result of rapid cooling after the welding. Also, due to the sufficiently high temperature, it produces coarse grain structures. The coarse grain HAZ is more hardenable and less ductile than the regions further away from the fusion boundary [5]. Therefore, this is the region where the greatest risk for cracking prevails. Hydrogen cracks, if present, are invariably found in this region. The cooling rate of a weldment depends upon the plate thickness, geometry, the heat input during welding and the initial temperature of the parts being joined. Control over the cooling rate can therefore be achieved by varying the heat input and the preheat temperature. The hardenability of a steel depends on the composition of the steel. Hardenability is best described by carbon equivalent (CE) which normalizes the contribution of all the alloying elements of steel to a solitary value. There are many empirical formulae for carbon equivalent which are given in a later section of this paper. Higher CE values usually denote higher hardenability, which in turn indicates a higher tendency of the steel to form a hard and crack susceptible microstructures [15]. In general, only hard HAZ microstructures are susceptible to HAC.

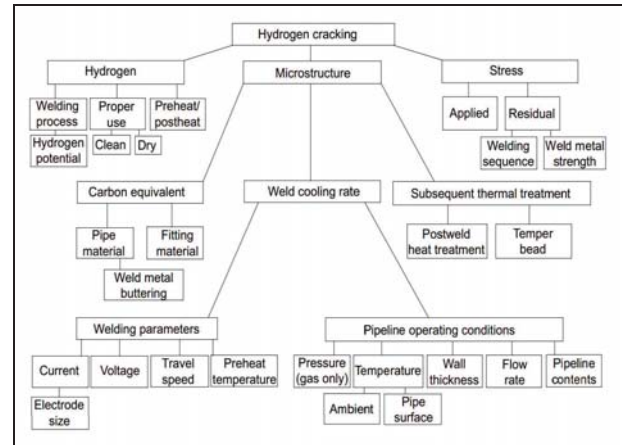


Fig. 4 Schematic representation of various factors influencing HAC [16]

The various factors influencing the three above necessary requirements to cause HAC are shown schematically in **Fig. 4**.

2.2 Mechanism of HAC in welds

It is now clear that HAC in a weldments may take place when sufficient amount of hydrogen, a high tensile residual stress and a crack susceptible microstructure coexist in the weldment. There are various mechanisms proposed for HAC [17-25]. However, none of these mechanisms explain HAC completely and there remains a wide disagreement concerning the exact mechanism [3, 4, 26, 27]. Summarizing these mechanisms, a sequence of events that leads to HAC of weld can be put forward as follows [5, 28]:

- Moisture available in the vicinity of welding arc atmosphere is dissociated to produce hydrogen molecules, hydrogen atoms and hydrogen ions.
- The hydrogen molecules, atoms and ions are dissolved in the molten weld pool.
- During the cooling and solidification of the weld metal, it becomes supersaturated with hydrogen.
- The supersaturated hydrogen in the weld metal has a propensity to migrate into the HAZ. If the HAZ is austenitic, hydrogen diffuses from the weld metal across the fusion line into the HAZ because austenite has a higher solubility for hydrogen. If the HAZ transforms before the weld metal, i.e., if the weld metal is austenite, hydrogen resides in the weld metal.
- While hydrogen is dissolved in the austenite weld metal or HAZ, during the rapid cooling, austenite is transformed into the crack susceptible martensite or bainite. Hydrogen, actually dissolved in the austenite, now remains in the martensite or bainite in a state of high energy.
- The high energy hydrogen seeks the defects and discontinuities in the lattices by diffusion, and is

accumulated there. The sites of hydrogen accumulation are known as traps.

- g. The residual tensile stress in the weldment, which is generated by the volume changes due to the transformation and is further complemented by any external restraint, acts with the accumulated hydrogen to enlarge the lattice discontinuities to crack size. The accumulated hydrogen may accelerates cracking by lowering the cohesive strength of the metal lattice. Once a crack is formed, it grows as hydrogen concentrates further.
- h. The crack growth carries the crack tip away from the point of hydrogen concentration. Hydrogen then diffuses to the crack tip to facilitate further crack growth.

The typical locations of the cracks in a weldment are shown in **Fig. 5**. Since hydrogen is one of the three factors responsible for HAC, it is necessary to either remove or reduce the hydrogen entering into the weld. Not all the hydrogen that enters into the weld is free to diffuse. Depending upon the temperature, a part of the absorbed hydrogen remains trapped in the various hydrogen traps available in the weldment. This part is known as residual hydrogen. The residual hydrogen content in a weld varies with the trap density which is a function of temperature. Residual hydrogen does not contribute to the cracking of the weld because it is not free to diffuse. The other part of absorbed hydrogen, which is free to diffuse within and out of the weldment, is known as diffusible hydrogen (H_D). Historically, it is accepted that H_D is responsible for the cracking because it is able to migrate. Therefore, it is necessary to gain a knowledge of the H_D content of a weld. The different sources contributing towards the hydrogen in the weldment and the behavior of hydrogen in the weld are discussed in the subsequent sections.

3. Source of hydrogen during welding

It is known that all the flux-bearing welding processes introduce some extent of hydrogen into the weld [10]. The sources of hydrogen in a welding process may differ from one process to the other. The sources are broadly classified into two categories, the major and the minor sources, based on the amount of hydrogen they contribute to the total hydrogen content of the weld metal.

Major source of hydrogen in a weld is the chemically bonded water/moisture in the electrode flux coating or core (SMAW or FCAW), powder flux (SAW) and hydrogen in shielding gas (GTAW and GMAW) [30-33]. The chemically bonded water (H_2O) in some ingredients forms an integral part of the flux. This water is often held by the strong ion-dipole interaction which is reported to be stable up to 1000°C [8, 30]. Therefore, hydrogen from this source can not be removed by baking the electrode at temperatures $\sim 300^\circ\text{C}$ (maximum temperature recommended for electrode baking). Apart from this,

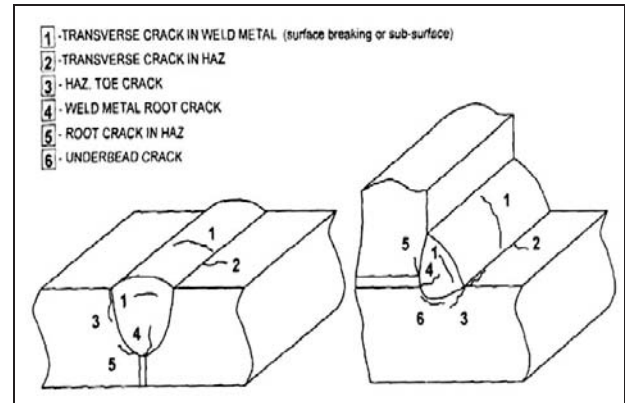


Fig. 5 Schematic illustration of typical crack locations associated with HAC in welds [29]

some incidental hydrogenous material on the electrode surface can also contribute largely towards the total hydrogen content of the weld. In SMAW, the cellulose and rutile coated electrodes produce large amounts of hydrogen in the arc atmosphere due to the dissociation of the cellulose [8]. McKeown has determined the moisture content in some of the common raw materials used in the manufacturing of welding consumables [30]. For this, the raw materials were first heated at 500°C for 1 h and their moisture content was determined by heating at 1000°C . The results are shown in **Table 1**. The moisture content in the electrode coating depends upon the moisture content of individual materials used in the electrode coating.

The minor sources of hydrogen in a weld include the moisture absorbed by the flux coating from the surroundings, hydrocarbon contaminants such as oil, primer, paint, grease etc., oxide layers on the base metal surface, atmospheric moisture absorbed by the powdery electrode core or the flux coating, residual hydrogen in the bulk of the base metal, moisture from the surrounding of the welding atmosphere [8, 34, 35]. Hydrogen can be readily reduced or eliminated from these sources by baking the electrodes at temperatures in the range of $100-350^\circ\text{C}$, proper cleaning of the base metal etc. The maximum allowed moisture contents for different welding electrodes and their baking conditions are given in **Table 2**.

Based on Sievert's solubility law, an empirical relation between the H_D content of a weld and the moisture content of the welding electrode used in the weld is given below [37, 38]:

$$H_D = \sqrt{\alpha^2(\eta_1 a_1 + \eta_2 a_2) + \beta^2 b} \dots (1)$$

For a condition of 50% of carbonate in a basic flux coating, equation 1 reduces to

$$H_D = \sqrt{260a_1 + 30a_2 + 0.9b - 10} \dots (2)$$

Where,

H_D : Diffusible hydrogen content

Table 1 Moisture content of raw materials used in the welding consumables [30]

Material	Moisture (%)	Material	Moisture (%)
Coarse limestone	0.09	Silica Sand	0.04
Fine limestone	0.09	Fine silica	0.12
Whiting	0.16	Rutile	0.01
Calcite	0.17	Fine rutile	0.02
Dolemite	0.18	Anatase	0.18
Feldspar	0.44	Fluorspar	0.09
Coarse feldspar	2.26	Coarse fluorspar	0.09
Fine feldspar	0.54	Bentonite	2.16
Mica	3.77	Albion clay	4.65
Fine mica	3.34	China clay	2.64

a_1 = The moisture of the coating after baking the electrode (measured as per AWS A5.5)

a_2 = The moisture absorbed by coating within the time interval between baking and welding

b (mm Hg) = The partial pressure of moisture in the ambient atmosphere

η_1 and η_2 = The efficiencies of moisture transfer from the coatings into the atmosphere

α = A constant indicating the activity of moisture in the coating on the hydrogen content dissolved into weld metal, (ml/100g*wt %)^{1/2};

β = A constant indicating the activity of humidity in ambient atmosphere on the hydrogen content dissolved into weld metal, in (ml/100g) (mm Hg)^{1/2}

It was seen that the chemically bonded water, a_1 of the electrode can be reduced to some extent by increasing the baking temperature during the manufacture. This reduces the diffusible hydrogen content to a greater degree [31, 38]. The absorbed moisture, a_2 depends upon the humidity of the atmosphere and the exposure duration. Hirai et al estimated that 100% moisture from the chemically bonded water of the basic flux coating enters the arc atmosphere as compared to 12% of the absorbed moisture [38]. From the above discussion, it is clear that the contribution of chemically bonded water in the coating to the diffusible hydrogen is significantly higher than that of the absorbed moisture.

4. Behavior of hydrogen in steel weldments

The diffusion of hydrogen from the weld metal to the HAZ and the development of cracks and the crack

Table 2 Recommended electrode baking conditions [36]

Type of coating	Electrode	Baking conditions	Maximum allowed moisture (%)
Cellulose	E6010	No baking	-
Rutile	E6013	No baking or 125°C/1 h	-
Basic	E70XX	250°C/2 h	0.4
Basic	E80XX	250 °C /2 h	0.2
Basic	E90XX	250 °C /2 h	0.15
Basic	E110XX	250 °C /2 h	0.15
Basic	E110XX	250 °C /2 h	0.1

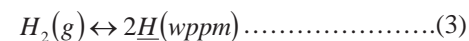
location in a weldment depend on the amount of hydrogen absorbed from the arc atmosphere, the solubility of hydrogen in the crystal structure, the diffusion and trapping of hydrogen in the steel lattice.

4.1 Solubility of hydrogen in weldment

It is known that hydrogen is absorbed in the weld pool from the welding arc atmosphere. Generally, the solubility of diatomic gases in liquid metals is described by Sievert's Law. However, Gedeon et al proposed a different model for specific to the solubility of hydrogen in steel weld [39]. Both the models are discussed below.

4.1.1 Application of Sievert's Law to predict the hydrogen solubility in steel welds

Sievert's law [40], in relation to the solubility of hydrogen in liquid steel, can be stated as follows: "In an isothermal and closed system, the equilibrium concentration of hydrogen gas (H_2) in a molten steel exposed to H_2 -atmosphere is proportional to the square root of the partial pressure of the diatomic gas above the melt". The equilibrium reaction is



And the corresponding equation for the equilibrium concentration of hydrogen in steel is

$$\bar{H} = K_s \sqrt{P_{H_2}} = \sqrt{P_{H_2}} \exp\left(-\frac{\Delta G_0}{RT}\right) \dots (4)$$

Where

\bar{H} = Equilibrium concentration of hydrogen dissolved in the molten steel

P_{H_2} = Partial pressure of hydrogen above the melt

ΔG_0 = Standard free energy of hydrogen dissolution in

steel

K_s = Equilibrium constant for the reaction, exponentially decreasing with temperature,

R = Universal gas constant

T = Temperature of the weld pool

In the absence of an electric arc, the Sievert's law holds good for the solubility of diatomic hydrogen and the equation (4) can be used to calculate the solubility limit of H_2 in the molten weld pool. It is often stated in the literature that the solubility of diatomic gases in the weld pool increases as the partial pressure of gas in the arc atmosphere increases, which follows the Sievert's Law.

4.1.2 Insufficiencies associated with the applicability of Sievert's Law in predicting weld hydrogen solubility

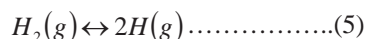
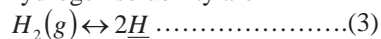
A careful analysis of literature data and experimental results reveal that the Sievert's law is insufficient to explain the solubility of hydrogen in steel during welding [39]. The major concern is that the Sievert's law does not consider the dissolution of monoatomic hydrogen and the ionization of hydrogen in the welding arc. Since the arc welding processes involve an electric arc, dissociation of diatomic hydrogen gas into monoatomic hydrogen and the ionization of hydrogen may be possible in the arc. Also, it has been shown that when a liquid metal is in contact with an arc plasma, the solubility of a diatomic gas is significantly higher than the level predicted by Sievert's law. The calculations based on Sievert's law yield a reaction temperature, the temperature on the weld pool surface during the absorption of hydrogen, much higher than 2500°C [41-45] which actually is reported to be the maximum surface temperature achievable in the arc welding of steel [46-50].

4.1.3 The solubility model by Gedeon et al [39]

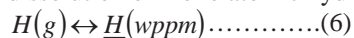
The Gedeon's model considers the effect of the electric arc plasma on the hydrogen solubility, the dissociation of diatomic hydrogen, H_2 into monoatomic hydrogen, H and the dissolution of monoatomic hydrogen in the weld pool. This model is based on the following two assumptions

- The temperature of the arc plasma is sufficient to cause the dissociation of H_2 into H .
- Absorption of H at the liquid metal interface

Following this model, the equilibrium reactions for the hydrogen solubility are



A combination of equation (3) and equation (5) is the dissolution of mono atomic hydrogen.



The change in free energy associated with the reaction in equation (6) is

$$\Delta G = -44.78 + 3.38T \dots\dots\dots(7)$$

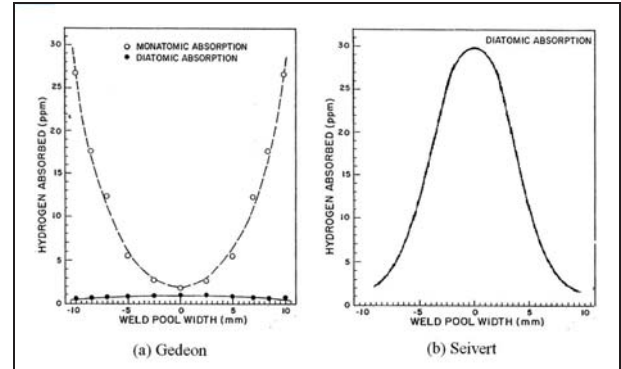


Fig. 6 Absorption of hydrogen in the weld pool [39]

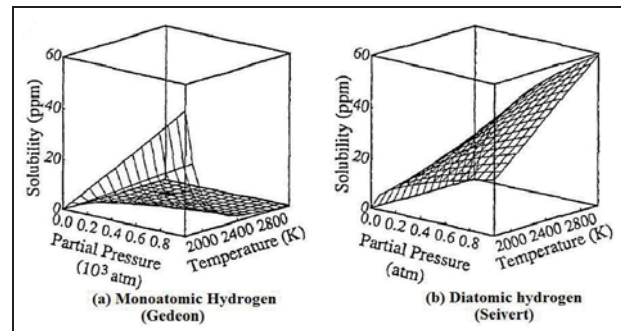


Fig. 7 Solubility of hydrogen in weld pool [52]

The solubility of the monoatomic hydrogen is different from that of the diatomic hydrogen. Equation (7) clearly shows that the free energy increases with an increase in the temperature. Therefore, the dissolution reaction would be reverted i.e., the solubility of hydrogen would decrease with an increase in weld pool temperature. This implies that the majority of monoatomic hydrogen absorption takes place at the cooler edges of the weld pool close to the fusion line as shown in Fig. 6 (a) [39, 50, 51]. This is in contrast to the predictions of Sievert's law owing to which the hydrogen absorption is maximum in the high temperature region of the weld pool directly under the arc as shown in Fig. 6 (b). The results in Fig. 6 (a) also show that the monoatomic hydrogen dissolution makes a dominating contribution to the total weld metal hydrogen content.

The solubility patterns of hydrogen as a function of temperature and partial pressure of hydrogen in the arc plasma are shown in Fig. 7 as predicted from both the models. The Gedeon's model predicts that, at a given reaction temperature, hydrogen solubility in the weld pool increases linearly as a function of the partial pressure of monoatomic hydrogen and decreases monotonically with an increase in the reaction temperature. As per the Sievert's law, the solubility of H_2 in the weld pool increases with an increase in the partial pressure of H_2 in the arc until a maximum solubility level is reached. At still higher partial pressures, the solubility remains unchanged. The solubility increases steadily as a function of temperature. A recent investigation [52] on the solubility of hydrogen in welds provided sufficient experimental and analytical support to Gedeon's model.

4.1.4 Hydrogen solubility in the various phases of steel

Solubility of hydrogen in steel depends upon the temperature, pressure, and the crystal structure of steel [53]. The variation in the solubility of hydrogen in the different phases of steel as a function of temperature and pressure is shown in **Fig. 8**. It is apparent from the figure that with increasing temperature, the solubility of hydrogen increases when ferrite (α) transforms to austenite (γ). The solubility drops when austenite transforms to delta-ferrite (δ). There is a sharp increase in solubility when the liquid phase is reached. In liquid iron, the solubility of hydrogen is reported to be as high as 34wppm at 1600°C and 1 atmosphere [54, 55]. When the liquid metal is rapidly cooled down to room temperature under nonequilibrium conditions, hydrogen retained in the steel can be much above the solubility limit since the solubility of hydrogen in steel at room temperature is quite low. In the martensite phase, this solubility of hydrogen is reported to be 0.4wppm, lower than that in the γ -phase but is higher than that in the α -phase (3×10^{-4} wppm) [56].

4.1.5 Weld hydrogen content

The steady state hydrogen concentration in a molten weld pool during welding can be predicted using a model proposed by Hooijmans et al [57]. In this model, it is assumed that the hydrogen concentration in the weld pool at any instant of time depends upon the inflow and outflow rates of hydrogen. The inflow of hydrogen into the weld pool is due to the hydrogen absorption across the arc-weld pool interface and due to the melting of the material in front of the weld pool. The inflow rate is determined from the arc conditions such as the concentration of hydrogen in the arc and the arc temperature. The outflow of hydrogen is due to the escape of hydrogen on the entire outer surface of the weld pool and also during its solidification. The outflow rate is proportional to the hydrogen concentration in the weld pool. Based on this, the time dependent change in the hydrogen concentration in the weld pool is described by the following equation:

$$\frac{dH}{dt} = W \left(\frac{dC}{dt} \right) = \alpha A - \beta B C + R_m C_0 - \eta R_m C \dots (8)$$

Where,

Hydrogen absorbed in the weld pool across the arc-weld pool interface = αA

Hydrogen inflow due to the melting of material = $R_m C_0$

Hydrogen escape from the weld pool surface = $\beta B C$

Hydrogen outflow due to weld pool solidification = $\eta R_m C$

H = Amount of hydrogen present in the liquid metal (g),
 t = Time (s),

W = Weight of the liquid metal in the weld pool (g),

C = Hydrogen concentration in the liquid metal (wt-%),

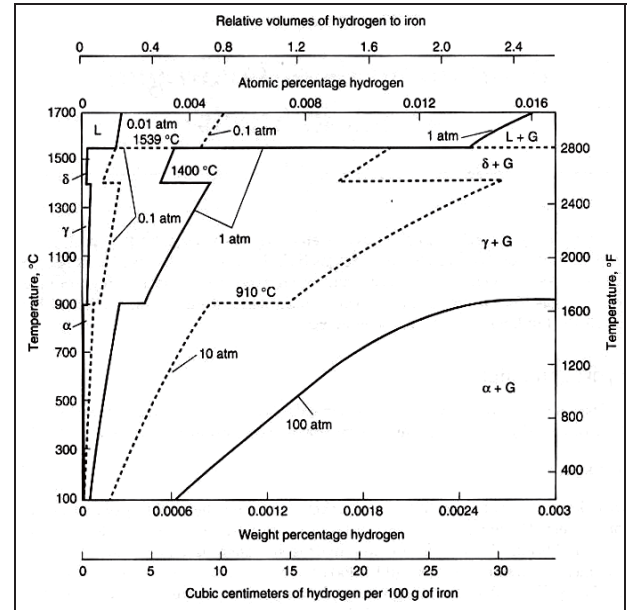


Fig. 8 Solubility of hydrogen in steel as a function of temperature and pressure [53]

α = Absorption coefficient (amount of hydrogen entering in the weld pool per unit area per unit time, $\text{g/m}^2\text{s}$),
 A = Interface area between the arc and the liquid metal (m^2),

β = Desorption coefficient (a proportionality factor depending on the temperature of the weld pool, $\text{g/m}^2\text{s}$),

B = Interface area between the weld pool and the surrounding gas atmosphere (m^2),

R_m = Melting rate (the amount of metal which melts per unit time, g/s) being equal to the solidification rate (the amount of metal which solidifies per unit time),

$$R_m = v s \rho$$

v = Travel speed (m/s)

s = Surface area of weld cross section (m^2)

ρ = Density of material (g/m^3)

C_0 = Original hydrogen concentration in the material (wt-%) and

η = Constant representing the fraction of the hydrogen frozen in during solidification.

The solution of the equation (8) is given in equation (9)

$$C(t) = \left(\frac{\alpha A + R_m C_0}{\beta B + \eta R_m} \right) \left[1 - \exp \left(- \frac{(\beta B + \eta R_m)}{W} t \right) \right] \dots (9)$$

After welding for a sufficiently long time, $\exp \left(- \frac{(\beta B + \eta R_m)}{W} t \right) \rightarrow 0$, therefore, the steady state concentration of hydrogen, C_e can be represented as

$$C_e = \left(\frac{\alpha A + R_m C_0}{\beta B + \eta R_m} \right) \dots (10)$$

Substituting $R_m = v s \rho$ and considering $\eta = 1$ (no hydrogen bubble formation) and $C_0 = 0$, Equation (10) reduces to

$$C_e = \left(\frac{\alpha A}{\beta B + v s \rho} \right) \dots \dots \dots (11)$$

The concentration of hydrogen in the weld pool at any instance of time can be predicted from the equation (11). The values of A, B, v, s and ρ can be measured directly. The determination of α and β is detailed elsewhere [58].

4.2 Diffusion of hydrogen in the weldments

It is known that hydrogen absorbed in the weld metal has a tendency to diffuse into the HAZ or out of the weldment. In a metal with no lattice defects, the diffusion of hydrogen can be described by Fick's non-steady state diffusion equation given below [59, 60]

$$\frac{\partial C}{\partial t} = D \nabla^2 C \dots \dots \dots (12)$$

Where, C = Concentration of hydrogen diffusing in steel

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} = \text{Laplace operator}$$

D = Lattice diffusivity of hydrogen

However, in a weldment, the diffusion of hydrogen is hindered by the trapping of hydrogen by the lattice defects called traps which are discussed in the next section. There are several factors which affect the lattice diffusion of hydrogen in steel. Bollinghaus et al have categorized the effects into three types, the trapping effects, the surface effects and the liquid state effects [61]. The factors affecting the lattice diffusivity of hydrogen in steel are shown schematically in **Fig. 9** [61]. Also, the scatterbands reported for the diffusivity of hydrogen in steel from a compendium of numerous literature data are close at higher temperatures whereas the scatter is large at lower temperatures where HAC is more likely [6, 61, 62]. These scatterbands are shown in **Fig. 10**. The higher scatter at lower temperatures may be because of the considerable trapping of hydrogen. Therefore, taking into account the effect of hydrogen trapping and the interchange of hydrogen atoms between the trapped and diffusing populations, a set of modified diffusion equations was proposed [63, 64]. The modified equations for the trap limited diffusion of hydrogen are given below

$$\frac{\partial C}{\partial t} + N \frac{\partial n}{\partial t} = D_{app} \nabla^2 C \dots \dots \dots (13)$$

$$\frac{\partial n}{\partial t} = k C (1 - n) - p n \dots \dots \dots (14)$$

$$D_{app} = \frac{D}{1 + \left(\frac{Nk}{p} \right)} \dots \dots \dots (15)$$

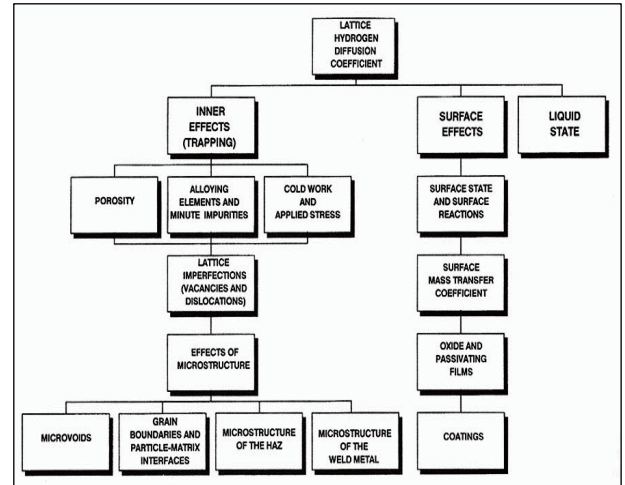


Fig. 9 Factors affecting the lattice diffusivity of hydrogen in mild steel [61]

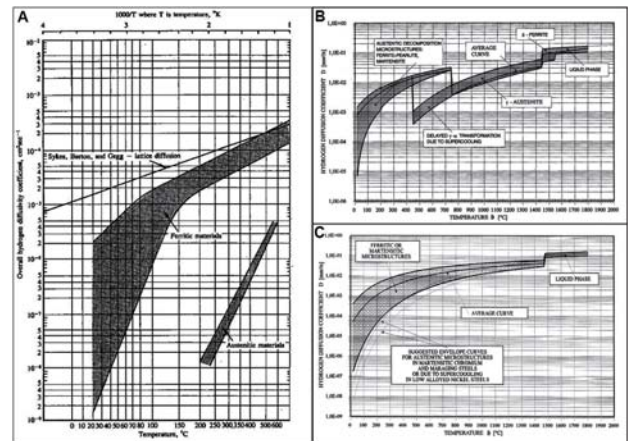


Fig. 10 Scatterbands for hydrogen diffusivity in (A) Ferritic and austenitic steels [6] (B) Microalloyed and low carbon steels [61] (C) Steel having ferritic and martensitic microstructure at room temperature [62]

Where,

C = Concentration of free hydrogen atoms

D = Diffusion co-efficient of hydrogen in the case of no trap sites

D_{app} = Apparent diffusion co-efficients of hydrogen by considering the trap sites

N = The trap site density per unit volume

k = The rate constant of capture in trap site

p = The rate constant of escape from the trap site

n = The coverage ratio of the trap sites

The equations (13-15) have been used to study the diffusion and distribution of hydrogen in steel welds [65, 66].

4.3. Hydrogen trapping in the weldment

Diffusion of the supersaturated hydrogen in the weldment may be impeded by traps present in the crystal structure. A trap is a barrier where hydrogen is preferentially retained and the activation energy required

to overcome this barrier is much higher than the activation energy of normal lattice sites otherwise occupied by hydrogen atoms. It is mentioned earlier that the hydrogen dissolved in a weldment is divided into two categories namely residual hydrogen, and diffusible hydrogen (H_D). Residual hydrogen is the amount of hydrogen trapped in the irreversible traps of the weldment. The irreversible traps offer higher binding energy for hydrogen ($|\Delta E_B| \geq 50 \text{ kJ/mol}$) [67]. Hence, high temperature ($\geq 600^\circ\text{C}$) is required to make the residual hydrogen released from the irreversible traps. Therefore, residual hydrogen can not diffuse at the lower temperatures at which HAC takes place and thus does not contribute to HAC. On the other hand, diffusible hydrogen is the amount of hydrogen trapped in the weak trap sites. The weak traps are classified under the category of very reversible traps [68, 69] and reversible traps [67]. Reversible and very reversible traps hold hydrogen with lower binding energies ($|\Delta E_B| \leq 30 \text{ kJ/mol}$). Hydrogen is able to escape from these traps even at lower temperatures (i.e., in the vicinity of 45°C) and is able to diffuse through the lattice. This hydrogen is called the diffusible hydrogen (H_D) which is considered to be potentially responsible for HAC. Different hydrogen traps, their corresponding binding energies and the associated hydrogen detrapping temperatures are shown in **Table 3**.

Apart from the classification given in **Table 3**, traps are classified into attractive traps, physical traps, repellers and obstacles on the basis of the kind of impedance they offer for hydrogen diffusion [71, 72]. Attractive traps exert an attractive force upon the hydrogen atom. Hydrogen atoms fall randomly into a physical trap. A repeller is a region which exerts a repulsive force for hydrogen. An obstacle is a region of discontinuity through which hydrogen cannot diffuse. It is noteworthy that attractive traps and repellers exert mutually opposite effects on hydrogen and so do the physical traps and obstacles. Schematic presentation of these traps is shown in **Fig. 11**.

5. Distribution of hydrogen in weldments

Hydrogen absorbed in the weld pool has a propensity to diffuse within the weldment. The diffusion depends upon the temperature, the alloy content/microstructure of the material, solubility, trapping and stress effects. Diffusion and accumulation of hydrogen in the heat affected zone (HAZ) of weldment has been first explained by Granjon [73] and is modified for carbon steels by Kou [74] based on the transformation temperatures of weld metal and HAZ in the weldment during welding. In the case of carbon steel welds, composition of the welding consumables is such that the microstructure of the weld metal in the as-welded condition is predominantly ferritic. However, the HAZ microstructure can be ferritic or bainitic or martensitic depending upon the composition and the cooling rate of the weldment during welding. Consider a typical case in

Table 3 Hydrogen trapping energies and detrapping temperatures [28, 70-72]

Hydrogen trap	Binding Energy (kJ/mol)	Detrapping Temperature ($^\circ\text{C}$)
Very Reversible Interstitial Lattice sites, Elastic stress field, Dislocations	≤ 7.7	30
Reversible Ti-Substitutional atom, Grain Boundary, Dislocation, Fe-C and Fe-Cementite Interface Martensite	17 - 36	112 - 270
Irreversible Microvoids, Inclusions and particle matrices like : Fe_2O_3 , Fe_3O_4 , MnS , Al_2O_3 SiO_2 , TiC , Ce_2O_3	37-112 129	305-750 >750

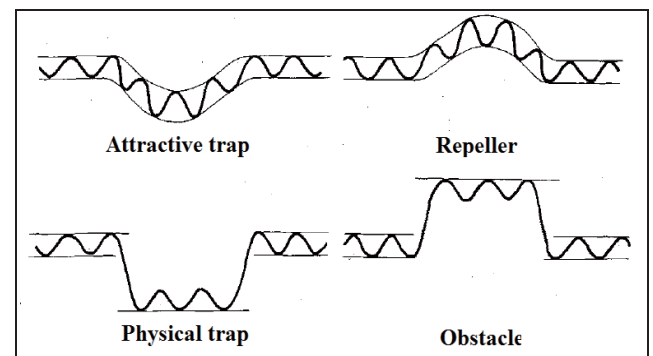


Fig. 11 Schematic representation of traps on the basis of their effect on hydrogen [72]

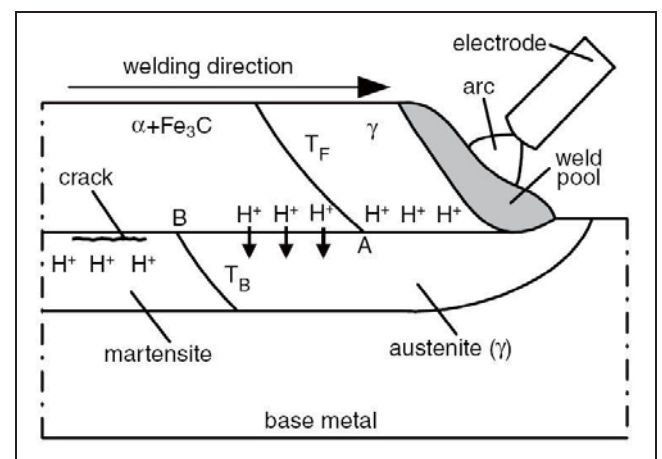


Fig. 12 Schematic representation of diffusion of hydrogen to HAZ [74]

which weld metal transforms to ferritic and HAZ to martensitic/ bainite. Transformation of austenite to ferrite occurs at higher temperatures (T_F) than the

transformation of austenite to martensite/bainite (T_B). As a result, during cooling of the weldment, weld metal transforms into ferrite at high temperature while HAZ still remains austenite as shown in **Fig. 12**

As the solubility of hydrogen in the ferrite is lower than that in the austenite, hydrogen is rejected from the weld metal ferrite to the HAZ austenite just adjacent to the fusion line. The higher diffusivity of hydrogen in ferrite also favors this process. The consequence of this is the accumulation of hydrogen in the HAZ adjacent to the fusion line. Upon the transformation of austenite to martensite, hydrogen solubility in the HAZ matrix decreases and the hydrogen becomes supersaturated in the HAZ. This re-distribution of hydrogen in the weldment due to the difference in the transformation behavior of weld metal and HAZ make the HAZ more susceptible to cracking than the weld metal in the case of carbon steel welds. The above concept is further verified by Wang et al [75] by calculating the hydrogen concentrations across the weldment. Nevertheless, the cracking need not always be confined to the HAZ in all the steel welds. In the case of alloy steels, composition of the welding consumables and the base metal are similar and hence transformations that occur in the HAZ and in the weld metal are similar. In such case, the hydrogen distribution within the HAZ and the weld metal may not differ much and hence both would be equally susceptible to cracking. In the case of high strength low alloy steels where the carbon content is reduced and strength of the steel is achieved by microalloying and microstructural modification using thermomechanical processing, both the HAZ and the weld metal remain ferritic [76, 77] and the weld metal is more susceptible to HAC than the HAZ. Locations of HAC in a weldment have been further studied by Matsuda et. al [78]. In their study, the variation of hydrogen concentration with time in the weld metal was assumed to be different than that in the HAZ, as shown in **Fig. 13**. This difference was attributed to the different thermal history of the weld metal as compared to the HAZ. The corresponding time dependent critical stress requirements for HAC in the weld metal and HAZ are shown in **Fig. 14**. It is clear that in case of a weld metal with lower hardness, the preferential site of HAC is the HAZ. This is because the stress level required for HAC in the weld metal is higher than that required for the HAZ. On the other hand, for a weld metal with high hardness, the crack will initiate in the weld metal because the critical stress required for HAC is met in the weld metal earlier than that in the HAZ.

6. Prevention of HAC in weldments

It is known that the risk of HAC in a weldment is improbable if one out of the three, crack susceptible microstructure, residual stress, and sufficient H_D content is absent or reduced. The residual stress and the hardenability of the weldment is difficult to control. Therefore, control over the H_D content is often preferred. As the main source of H_D in a weldment is the total moisture content of the coating of welding electrode,

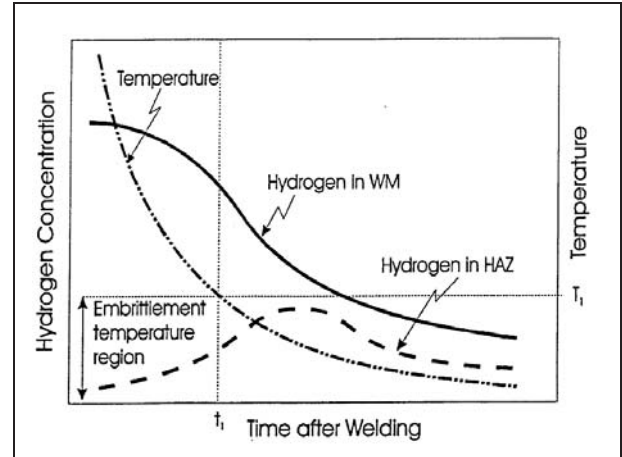


Fig. 13 Variation in the hydrogen content of the weld metal and HAZ after welding [78]

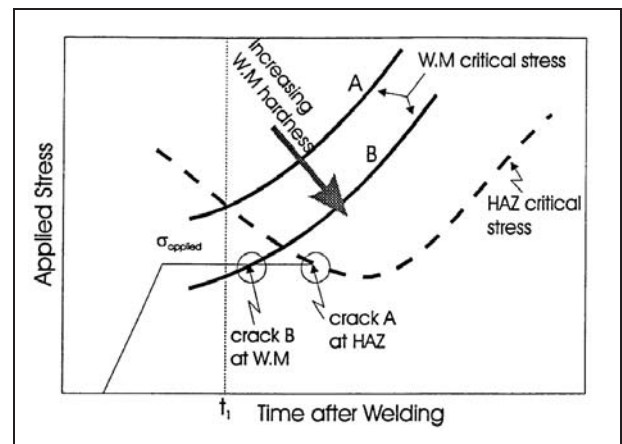


Fig. 14 Variation in stress in the weld metal and HAZ as a function of time after welding [78]

(A): Low W.M. Hardness, crack location is in the HAZ.
(B): High W.M. Hardness, crack location is in the weld metal (W.M.)

hydrogen absorbed can be reduced to some extent by baking the electrodes. However, the electrode coatings are hygroscopic and quickly pick up moisture from the ambient. Also, electrodes with cellulose coating produce a hydrogen rich gas shield in the welding arc. Therefore, cellulose coated electrodes are not used for the welding of steels susceptible to HAC.

Probably, reducing the cooling rate of the weldment is the most practical way of reducing the risk of HAC. Slow cooling of the weld provides more time for hydrogen in the weld to diffuse out. The slow cooling rate also facilitates the formation of ferritic and pearlitic microstructure, which are less susceptible to HAC, than martensite or bainite. Increasing the weld heat input is one of the ways to reduce the cooling rate of the weld; but this may have an adverse effect on mechanical properties of the weldment. Hence, the simplest and the most widely used technique to reduce the risk of cracking is to preheat the parts to be welded. Preheating reduces the cooling rate of the weldment after welding [79, 80].

There exists two methods which are adopted to estimate safe preheat temperatures to be employed in the welding of steels. One of these methods, known as the hardness control approach, considers the importance of changing the microstructure or hardness of HAZ from more susceptible to less susceptible. The other method, known as hydrogen control approach, lays emphasis on the reduction of H_D content. The choice of an approach depends upon the carbon and alloy content of the steel. In the studies related to HAC, the influence of various alloying elements on HAC is drawn into a single factor known as carbon equivalent (CE). The carbon equivalent is regarded as the normalized carbon content of the steel [81]. There are several ways of estimation of carbon equivalent proposed by various investigators which are valid under different ranges of composition of steels. In general, with an increase in the CE, the susceptibility to HAC increases. It is interesting to note that with an increase in the alloy content, the CE increases and steels even with low carbon content and high alloy content would be susceptible to HAC.

A classification diagram proposed by Graville, in which carbon content of a steel is plotted against CE is used to explain the choice between hardness control and hydrogen control approaches for choosing preheat temperature [6, 82]. This diagram, shown in Fig. 15 places different classes of steels in three different zones of the diagram based on their carbon content and CE. From this figure, one can find out the susceptibility of various steels to HAC as well as the approaches to be chosen for its prevention. Steels falling in Zone I have least susceptibility to HAC. Steels falling in Zone II have a high carbon content and low CE (low alloy content) and for these steels hardness control approach is used for selection of preheat temperature. This considers four factors, the combined thickness, the hydrogen content of welding electrode, the carbon equivalent and the weld heat input to arrive at a minimum preheat temperature that would prevent cracking. For steels in this zone, HAZ hardness can be varied by changing the heat input and preheat temperature. For steels falling in Zone III, CE and carbon content are high as a result, weld microstructure is always susceptible to HAC, Application of preheating or increasing the weld heat input can not alter the microstructure; hence, the only option to avoid HAC is to ensure that diffusible hydrogen in the weld is below the level required for cracking. Hence, hydrogen control approach is adopted for steels falling in this zone.

A higher preheat temperature would play a role of an external restraint and would complement the residual stress in the weld joint. This would favor HAC [83-86]. However, the choice of a safe preheat temperature is an intricate task. Various studies have proposed different cracking parameters to determine safe preheat temperatures for different steels and welding conditions [87-105]. These investigations mostly employed a unique parameter called cracking parameter to calculate A suitable preheat temperature. The empirical relation between diffusible hydrogen and preheat proposed in the

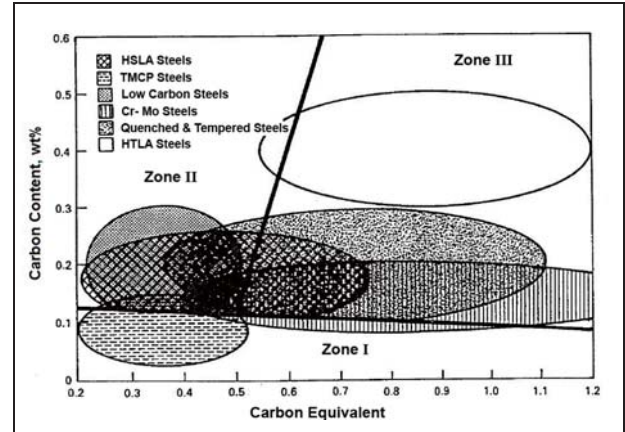


Fig. 15 Classification of steels to choose between hardness or hydrogen control approach to determine safe preheat temperature [82]

various investigations are given below investigations are given in Table 4.

In the Table 4,

$T_{preheat} (^{\circ}C)$ = Preheat Temperature

$$P_C(\%) = P_{cm} + \frac{H_{JIS}}{60} + \frac{t}{600} = \text{Ito-Besyo cracking parameter}$$

$$P_W(\%) = P_{cm} + \frac{H_{JIS}}{60} + \frac{R_F}{40000} = \text{Root cracking parameter}$$

$$P_H(\%) = P_{cm} + 0.065 \log H_{JIS} + \frac{R_F}{40000}$$

= Cracking parameter

$$P_{HA}(\%) = f(H_{JIS}) = f(H_{IW})$$

= Hydrogen accumulation parameter

$$P_{cm}(\%) = C + \frac{Si}{30} + \left(\frac{Mn + Cu + Cr}{20} \right) + \frac{Ni}{30} + \frac{Mo}{15} + \frac{V}{10} + 5B$$

= Ito-Bessyo carbon equivalent

$t(mm)$ = Plate thickness

$$R_F \left(\frac{Kg}{mm^2} \right) = \text{Intensity of tensile restraint}$$

$t_{(100)cr}$ = Critical time for weld to cool down to 100°C

$$CI = CE + 0.15 \log H_{JIS} + 0.3 \log (0.017 K_t \sigma_w)$$

= Cracking index

$$CE(\%) = C + A(C) \left(\frac{Si}{24} + \frac{Mn}{6} + \frac{Cu}{15} + \frac{Ni}{20} + \frac{Cr + Mo + Nb + V}{5} + 5B \right)$$

= Yurioka's carbon equivalent

$$CET(\%) = C + \left(\frac{Mn + Mo}{10} \right) + \left(\frac{Cr + Cu}{20} \right) + \frac{Ni}{40}$$

= Uwer's carbon equivalent

Table 4 Cracking parameters proposed for the calculation of preheat

Studies	Empirical relations for preheat
Ito and Bessyo [87, 88]	$T_{Preheat} (^{\circ}C) = 1440P_C - 392$, $T_{Preheat} (^{\circ}C) = 1440P_W - 392$
Suzuki et al [89-94]	$T_{Preheat} (^{\circ}C) = 1600P_H - 408$; $T_{Preheat} (^{\circ}C) = 146P_{HA}$, $T_{Preheat} (^{\circ}C) = 181P_{HA} - 16$ (For single pass weld)
JSSC Procedure [95]	$t_{(100)cr} = 105000(P_W - 0.276)^2$
Yurioka et al [96, 97]	$T_{Preheat} (^{\circ}C) = f(t_{(100)cr})$ (Graphically-calculated); $t_{(100)cr} = 67.6CI^3 - 182CI^2 + 163.8CI - 41$
Yurioka et al [98, 99]	$T_{Preheat} (^{\circ}C) = 120 + 120 \log \left(\frac{H_{JIS}}{3.5} \right) + 5(h_w - 20) + \sigma_8 - 83$; $(20 \leq h_w \leq 30mm)$
	$T_{Preheat} (^{\circ}C) = 120 + 120 \log \left(\frac{H_{JIS}}{3.5} \right) + 5(h_w - 20) + 8(\sigma_8 - 83) - 0.05(h_w - 30)^2$; $(30 \leq h_w \leq 40mm)$
Hart [100]	$T_{Preheat} (^{\circ}C) = 188.4CE_W - 108.3$
EN 1011-2 B/Uwer [99, 101, 102]	$T_{Preheat} (^{\circ}C) = 700CET + 150 \tanh \left(\frac{t}{35} \right) + 62H_{DIN}^{0.35} + (53CET - 32)Q - 330$
AWS D1.1 method [99, 103]	$SI = 12P_{cm} + \log H_D$

$$CE_w = C - 0.378Mn + 0.145Ni + 0.468Cr + 0.299Mo + 0.039H_2 - 0.012\Delta t_{800-500}$$

$$A(C) = 0.75 + 0.25 \tanh\{20(C - 0.12)\}$$

K_t = Stress concentration factor

σ_w (Kgf / mm²) = Mean stress acting on the weld

σ_8 (Kg / mm²) = UTS

h_w = Throat depth of the weld metal

Q = Heat input (kJ/mm)

H_D == Diffusible hydrogen content of weld metal (ml/100g)

H_{JIS} = H_D content (ml/100g) measured as per JIS Z3113 (Glycerin method)

H_{IIW} = H_D content (ml/100g) measured as per ISO 3690 (Mercury method)

H_{DIN} = H_D content (ml/100g) measured as per DIN 8572

$$H_{JIS} = 0.67 H_{IIW} - 0.8$$

Summarizing the relations in the Table 4, it can be concluded that the preheat temperature is a function of the diffusible hydrogen content of the weld.

$$\text{i.e. } T_{\text{Preheat}} (^{\circ}\text{C}) = f(H_D) \dots \dots \dots (16)$$

In other words, knowledge of H_D levels provides the starting point to determine safe preheat temperature. This fact constitutes the primary motivation for the determination of the H_D content of weld metal.

7. Classification of H_D in welding consumables

As the welding consumables are the major sources of hydrogen in steel welds, they are classified by various national and international standards based on the diffusible hydrogen that they can introduce into the weld metal [106-109]. Although these standards have many similarities in definitions and formulations for calculating the hydrogen levels, historically these have adopted different hydrogen levels, as given in **Table 5**.

It should be noted that, while IIW adopted a linear scale increment of hydrogen levels by units of 5 (5-10-15 ml/100g), AWS uses logarithmic scale (4-8-16 ml/100g) based on the correlation of diffusible hydrogen levels with critical cracking stress, critical preheat temperature, and the like, for avoiding hydrogen cracking [55]. From these correlations, the AWS logarithmic system of hydrogen classification is claimed to be more logical than the IIW linear system of hydrogen classification.

Table 5 Classification of consumables based on H_D content [55]

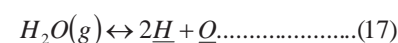
Type of Hydrogen Control	Weld metal diffusible hydrogen (ml/100g)			
	ISO 2560 & IIW	AWS A 5.1	AS/NZ S 3752	JIS Z 3211* & JIS Z 3212
Very low	≤ 5	≤ 4 $\leq 2^{\dagger}$	≤ 5	≤ 6 (780MPa)
Low	≤ 10	≤ 8	≤ 10	≤ 7 (750 MPa) ≤ 9 (610 & 690 MPa) $\dagger \leq 10$ (570 MPa)
Medium	≤ 15	≤ 16	≤ 15	≤ 12 (520 MPa) \dagger ≤ 15 (420* & 490 MPa)
High	> 15	> 16	-	-

\dagger Tensile strength of steel (MPa), \ddagger under consideration

Unlike the AWS and IIW, Japanese standards, JIS Z 3211 (for mild steel electrodes), and JIS Z 3212 (for high tensile strength electrodes) establish a single maximum diffusible hydrogen limit for each tensile strength level. However, in these standards, the step from low to very low H_D levels differ by 1 ml/100g of hydrogen content with a decrease from ≤ 7 to ≤ 6 ml/100g. Considering the reproducibility of the diffusible hydrogen tests to be ± 1 ml/100g, JIS scale seems impractical [110]. Regardless this factor, H_D content is an essential variable in standards like ANSI/AWS D1.1-2000 and AS/NZ S 1554.1-2000.

8. Control of H_D in welding consumables

It is known that the moisture in the electrode coating is mainly responsible for the hydrogen in the weld metal. In general, when water is heated above 1500°C, it forms hydrogen atoms [111, 112] following the reaction given below



\underline{H} and \underline{O} are the concentrations of hydrogen and oxygen in the solution.

From equation (17), it is clear that, the oxygen dissolved in steel has a profound effect on the hydrogen

dissolution. For the same amount of moisture content, more hydrogen is dissolved in the weld metal of a highly deoxidized steel than that of a high oxygen steel. In a basic SMAW electrode with carbonate, the water /gas reaction is



For the equilibrium of the reaction, a factor F is calculated which helps in predicting the effects of adding moisture to the arc atmosphere [113].

$$F = 1 - \left(P_{H_2} \times P_{H_2O} \right) \left[\frac{1}{P_{H_2}} + \frac{1}{P_{H_2O}} + \frac{1}{P_{CO}} + \frac{1}{P_{CO_2}} \right] \dots\dots(19)$$

In the equation 18, when F is positive, it's a high CO/CO₂ system. In this case, the addition of more moisture would result in increasing the partial pressure of hydrogen which would result in more hydrogen absorption. A negative F means for a low CO/CO₂ system. In this case, the addition of moisture would reduce the partial pressure of hydrogen in the arc atmosphere. This results a decrease in the hydrogen content.

As discussed earlier, a major part of hydrogen in the weld is the welding consumable. In SMAW, the coating used in the welding electrodes is responsible for the hydrogen in the weldment. With the increasing concerns of hydrogen related weld defects and the available available hydrogen benchmarks, the development of low hydrogen electrodes has been taken up by the electrode manufacturers. In the low hydrogen electrodes, the coating is formulated with ingredients that lack hydrogen in their chemical composition. This is primarily accomplished by eliminating the organic and chemical compounds high in moisture content [114]. A high temperature bake cycle is entailed in the electrode manufacturing process to remove the moisture. In this, after the coating is extruded onto the electrode core, the low hydrogen electrodes are initially baked at 150-370°C, followed by a rebake at 370-450°C for a specified period of time. The above procedure practically eliminates all the moisture. To prevent any moisture reabsorption from the atmosphere, the electrodes are immediately packaged in hermetically sealed metal containers following the high temperature bake.

8.1 Storage and Reconditioning of electrodes and moisture resistant coating

Moisture absorption by the welding electrode is of special concern in the places with a high level of relative humidity. The low hydrogen electrodes have a tendency to absorb moisture if exposed to the atmosphere. In such case, these electrodes are generally rebaked as recommended by the manufacturer, generally 250°C for 2 h. After rebaking, these electrodes are stored in a vented oven at a constant temperature of 50-60°C until they are used for welding.

As the temperature and relative humidity increase, the chance of absorbing moisture in the low hydrogen coating is greatly increased. To combat this possibility, major electrode manufacturers have in recent years

developed low hydrogen electrodes with moisture resistant coatings [115, 116]. These coatings reduce the rate of moisture absorption in electrodes that have been exposed to the air for extended periods, thus adding an extra degree of reliability to low hydrogen electrodes.

8.2 Hydrogen control by arc chemistry modification

In addition to the above, it has been reported that the H_D content of the weld metal in SMAW, SAW and FCAW processes can be manipulated through arc chemistry modifications [4, 117-123]. Modifications in the arc can be brought about by modifying the flux of the electrode. The above studies conclude that a careful addition of oxidizing ingredients like fluoride or calcite reduces the diffusible hydrogen content in welds. Apart from this, diffusible hydrogen content in the weldments can be considerable reduced by adding yttrium or neodymium as ferro-powders in the metal core of welding consumables [124]. Retained austenite in the weldment also acts as hydrogen trap and reduces the hydrogen content of weld [125].

9. Methods for the determination of H_D in weldments

The above discussed facts brings to the fore the need to measure diffusible hydrogen in weldments. Since HAC takes place in the weld metal as well as in the HAZ, diffusible hydrogen measurement in the weldment is generally preferred over that in the weld metal. There are several methods for the determination of diffusible hydrogen in weldments. Among these, only four methods are recommended by various standards such as IIW/ISO [126], AWS [127], BS [128], JIS [129, 130], DIN [131], AS/NZ [132], GOST [133] and BIS IS [134]. These include glycerin method, mercury methods in which collection and measurement of hydrogen is carried out at room temperature, and gas chromatography method and/or carrier gas-hot extraction method and vacuum hot extraction methods for the rapid determination of H_D. The determination of H_D involves three parts.

1. Preparation of weld specimen
2. Collection of H_D from the weld
3. Measurement of diffusible hydrogen

9.1 Preparation of weld specimen

The preparation of specimen is briefly described here. The detailed description of specimen preparation is available in the standards mentioned earlier [126-134]. Generally, for diffusible hydrogen measurement, a test assembly is prepared which consists of a specimen piece of dimension 30×15×10mm and run-on and run-off pieces of dimensions 45×15×10 mm. The test assembly is degassed at 650°C for 1 h to remove any bulk hydrogen and cooled in the furnace. Their surfaces are ground to remove the oxide scale formed during degassing treatment. These are finished at right angles to ensure good contact between the adjacent pieces, cleaned with acetone followed by warm air and stored in desiccators until they were used for welding. During welding, the specimen is placed in between the run on and run off

pieces. The run-on piece is used for arc striking and run-off piece for arc extinction during welding so that a stable arc and uniform shape of the deposit can be obtained on the specimen. The specimen is welded using prebaked welding consumables as discussed in the earlier sections. The welding is carried out by placing the test assembly on a welding fixture, a copper jig. The dimensions of the jig are such that during welding, the heat is immediately conducted away from the test assembly to the copper jig. A photograph of copper jig holding the test assembly is shown in **Fig. 16**. The schematic of a test assembly after deposition of the bead is shown in **Fig. 17**.

Immediately after the welding, the test assembly is quenched down to -78°C or less. The run-on and run-off pieces are broken off from the specimen. The specimen is stored at -78°C or less until it is used for H_D measurement. The various methods recommended for the collection and measurement of H_D are discussed below.

9.2 Collection and measurement of diffusible hydrogen

9.2.1 Glycerin Method

Glycerin method is probably the oldest method used for the determination of H_D in welds. Principle of measurement of H_D using this method is the displacement of glycerin by hydrogen and the subsequent volumetric measurement of H_D . Measurement using this method consists of two parts: preparation of weld specimen and collection of hydrogen evolved from the specimen over glycerin. In this method, four test specimen blanks, each of dimensions $125 \times 25 \times 12 \text{ mm}^3$ are used [130]. A single bead is deposited along the length of 25 mm with a total of 100mm for four specimens. The deposition is made using a prebaked 4mm diameter and 150mm long electrode. The welding conditions are short arc and a welding current of 150A. Immediately after deposition, samples are quenched in water at approximately 20°C and individual specimens are separated. They are stored in dry ice or liquid nitrogen until measurement.

For the measurement of H_D , each specimen is introduced in an apparatus containing glycerin as shown in **Fig. 18**. Glycerin is maintained at 45°C and hydrogen is collected from the weld sample for 48 hours. Hydrogen evolved from all the four specimens is collected simultaneously in four different apparatus. The amount of gas collected over glycerin is measured to the nearest 0.05 ml and the average estimated is corrected for STP using the following relation:

$$H_{\text{GLYCERIN}} = (V_t) \left(\frac{273}{273 + T} \right) \left(\frac{P}{760} \right) \left(\frac{100}{W_f - W_i} \right) \frac{\text{ml}}{100\text{g}} \dots (20)$$

Where,

H_{GLYCERIN} = Diffusible hydrogen measured using glycerin method

V_t = Volume of hydrogen measured at temperature T and pressure P

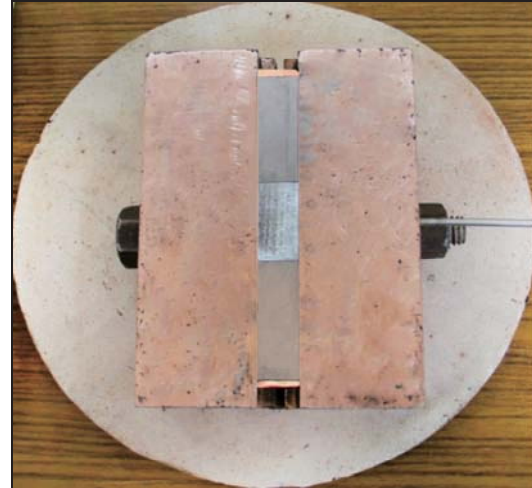


Fig. 16 Photograph of copper jig holding the test assembly

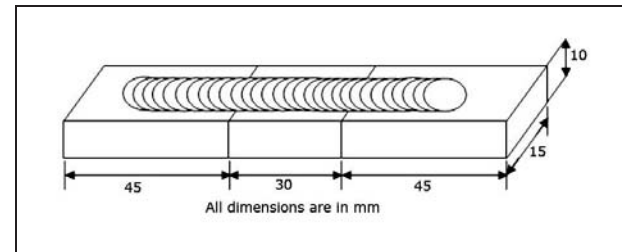


Fig. 17 Schematic of test assembly

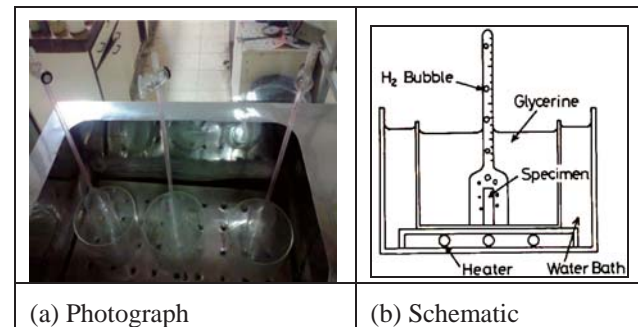


Fig. 18 Glycerin apparatus for diffusible hydrogen measurement

W_i = Weight specimen before welding

W_f = Weight of specimen after welding

The glycerin method was first introduced in the AWS Specification A5.5-48T (ASTM A316-48T) in 1948 [37, 38, 55, 135]. Shortly after its introduction, Stern *et al* suspected the suitability of glycerin as a hydrogen collection medium [136] because more hydrogen was collected over mercury than that over glycerin from similar weld specimens. The lower hydrogen content over glycerin were attributed to the fact that hydrogen is partially soluble in glycerin. Therefore, this method was removed from the AWS A5.5 specification. Also, many

other drawbacks which revolved around the reproducibility of this method. It was reported that the dissolution of water vapor, oxygen and nitrogen in glycerin which would contribute to the total gas collected. This method yielded varied hydrogen contents with the changes in the purity and viscosity of glycerin and with varied shapes of glasswares [137]. Therefore, it was concluded that, this method is not suitable for the measurement of lower levels of hydrogen because of significant loss of hydrogen, underestimation and wide scatter (50-90%) in the measurements [135, 138,139]. However, this method is still in use by the American bureau of shipping [140, 141].

9.2.2 Mercury Method

The principle of hydrogen measurement using the mercury method is the displacement of mercury by hydrogen and the subsequent volumetric measurement of hydrogen. The materials, apparatus, procedures for specimen preparation, H_D collection and its analysis using this method are detailed in many standards mentioned above [126, 127]. Historically, the eudiometers used for the collection of H_D in mercury method are either U-shape or Y-shaped. The schematics of the eudiometers are shown in **Fig. 19**. For measurement, the weld specimen, after quenching and cleaning, is admitted through the open limb into the Y-tube of the mercury apparatus and the limb is closed. The weld specimen is moved to the graduated close limb of the Y-tube with the help of a magnet. At this point, the Y-tube along with the weld specimen is evacuated by a suction/rotary pump. After evacuation, the vacuum is released and the initial reading in the graduated limb of the Y-tube is recorded. The Y-tube was evacuated again and the weld specimen inside is allowed to evolve hydrogen for 72h, and final reading is recorded. The difference between the initial and final readings is equal to the volume of H_D . From the weight of deposited metal, ambient temperature and pressure, collected hydrogen volume is converted into volume of hydrogen at standard temperature and pressure in ml/100g of deposited metal using equation (20). The volume of gas collected over mercury is corrected for STP conditions and reported in ml per 100 grams of deposited metal. Three such measurements are carried out simultaneously in three Y-tubes as shown in **Fig. 20** and the average H_D content is reported as given below.

$$H_{\text{MERCURY}} = (V_F - V_I) \left(\frac{273}{273 + T} \right) \left(\frac{B - H}{760} \right) \left(\frac{100}{W_F - W_I} \right) \dots (21)$$

In the above relation,

H_{MERCURY} = H_D measured by the mercury method at STP (ml/100g of deposited metal)

V_I = Initial volume of gas in the burette of Y-tube

V_F = Final volume of gas in the burette of Y-tube

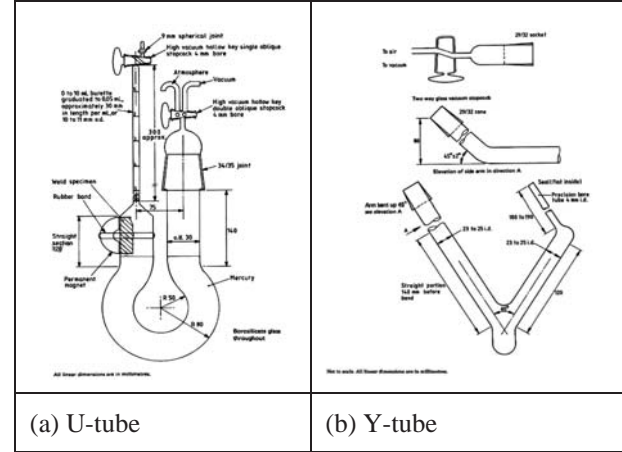


Fig. 19 Schematic of mercury eudiometers used H_D measurement



Fig. 20 Mercury apparatus used for H_D measurement

T = Temperature at which measurement is carried out

$W_F - W_I$ = Weight of the deposited metal

B = Ambient pressure reading in the Barometer

H = Mercury head, i.e., Difference in the heights of mercury levels in the two limbs of Y-tube at the end of measurement

With the disqualification of glycerin method as a standard for H_D measurement in welds, mercury has become the obvious choice as a hydrogen collection medium [135, 142] because hydrogen has virtually no solubility in mercury. Following the accuracy, reliability and reproducibility of results in the collection of hydrogen over mercury, this method was adopted as a standard method for the first time in the standard ISO 3690:1977 [55]. Despite several issues associated with the use of mercury, this method is retained in the recent revision of IIW, ISO 3690:2012 and is recommended by several other standards like AWS A4.3, AS/NZ S3572, BIS IS 11082, DIN 8572. This method is recommended as the primary standard/reference for H_D measurement. Any new method to be used as an alternative method for H_D measurement must show good correlation with the

mercury method [126]. The major difference in the mercury method in ISO 3690:1977 and ISO 3690:2012 is the increase in the time of hydrogen collection from 3 days to around 15-21 days (It is recommended that the collection of hydrogen must be continue until there is no increase in the calculated volume of hydrogen for H_D measurements on successive days. This can be achieved by continuing the hydrogen collection for 15-21 days). This change was based on a study by Jenkins et al [111] which found that the H_D contents obtained from 3 day measurements show poor reproducibility and are consistently lower than those obtained for a 21 day measurement at room temperature. However, with a fear of possible health hazards associated with the handling of mercury, the temperature used for hydrogen collection was initially confined to 25°C; later extended up to 45°C by incorporating sealings for mercury [126, 127]. Still, this method is not allowed in many countries. Another drawback of this method is the time consuming hydrogen collection (for 3-21 days). Recently, it was suggested that hydrogen collection from the weld in mercury can be carried out at temperatures up to 180°C with reduced safety concerns by incorporating several modifications to the mercury eudiometer design and sealing [143]. However, no further developments are reported in the literature regarding the implementation or consideration of these modifications.

9.2.3 Gas Chromatography Method

With the increasing demand for batch production of welding consumables, there was an urgent need for the quality control to reduce the minimum 3 day requirement for H_D collection to reasonably lower times. This required adoption of techniques with provisions of heating the weld to accelerate the evolution of hydrogen. Gas chromatography (GC) was one such method which provided facilities for heating the weld specimen in a hydrogen collection in a chamber up to 150°C [55, 144-146]. Since the weld specimen was heated at an elevated temperature, the collection of hydrogen from the weld specimen is accomplished within 6 h. Therefore, in the GC method, the time duration of H_D measurement was reduced from 3 days to 6 h [11]. In the mid 90's, Oerliken-Yanaco marketed an H_D analyzer (**Fig. 21**) which was widely used by the welding consumable manufacturers. At present, this method is recommended by various standards, ISO 3690: 2012, AWS A4.3-93, AS/NZ S3752, JIS Z 3118, etc.

In the GC method used for H_D measurement, the gas chromatograph is provided with a thermal conductivity detector (TCD) for the analysis of hydrogen collected. For hydrogen collection, initially, no temperature higher than 150°C was considered for H_D collection because of two reasons. First there was an issue with the oxidation of specimen surface at still higher temperatures. Surface oxidation is known to slow down the hydrogen evolution from the weld specimen [139, 147, 148]. Second, there was suspicion about the release of residual hydrogen which would lead to an overestimation of diffusible

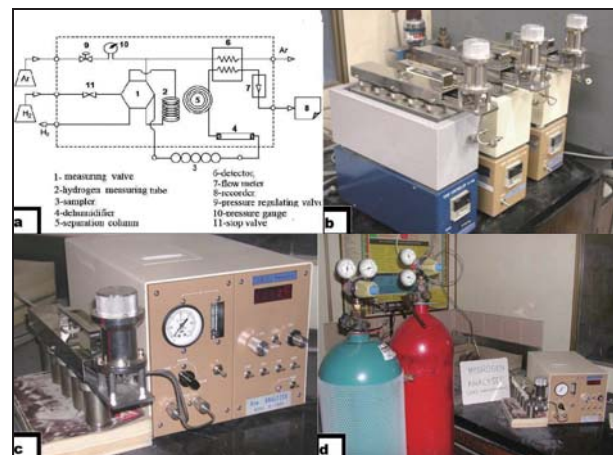


Fig. 21 Oerliken-Yanaco GC setup for H_D measurement (Photo Courtesy: [110])

- a) Flow Diagram of GC apparatus
- b) Electric Furnaces to heat chamber
- c) Chambers Connected to GC analyzer
- d) Carrier gas connected to GC analyzer

hydrogen [149]. H_D from weld specimen is collected by holding the weld specimen in a separate closed chamber. In gas chromatography, an aluminium or steel chamber (**Fig. 22**) is used for collection [150]. After collection of H_D , its analysis is carried out using a thermal conductivity detector (TCD).

The detailed description of H_D measurement using this method is given elsewhere [151-153]. In general, gas chromatography involves the separation of a mixture of gases in its column. It detects the individual gases in a gas mixture. The separation of individual gases is achieved on the basis of their retention time in the stationary phase of the GC column. Retention time is the time for which a gas is retained in the column. For a given column, different gases have different retention times. Therefore In a gas mixture, different gases reach the detector, TCD at different times. In the H_D measurement, a carrier gas such as pure argon accompanies the hydrogen collected in the collection chamber to the TCD. TCD setup has four Tungsten-Rhenium alloy filaments connected in two channels in a Wheatstone bridge configuration. During the analysis, these filaments are heated to a particular temperature. When different gases are passed across the channels, heat is lost and each channel will experience a temperature drop depending upon the thermal conductivity of the gases. The temperature gradient across the channels induce a change in the filament resistance. The principle of gas analysis using the TCD is the measurement of the change in resistance. For H_D measurement, initially a baseline is set by flowing the same gas (reference gas) across both the channels. Later, H_D collected in the chamber is injected through the GC column. In this situation, hydrogen gas flows across one of the channels and the reference gas across the other. This produces a change in resistance and a net output voltage (V_{out}) which is displayed as a peak. The area

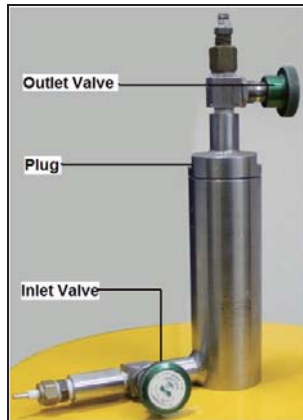


Fig. 22 Chamber used for the collection of diffusible hydrogen

under the peak is proportional to the volume of the sample gas. A typical hydrogen peak from GC is shown in **Fig. 23**

Though this method is comparatively faster than the mercury method and the results obtained using this method agrees well with mercury method, there are still several limitations. The results obtained using this method are affected significantly by factors such as the incomplete purging of the collection chamber, traces of moisture in the carrier gas and moisture contamination in the dehumidifier or in the GC column [11, 39, 152]. Also, this method demands calibration before each analysis [11, 39]. Although the H_D measurement using this method is completed within 6 h, with the increased demand for quality control and batch testing for product release still shorter analysis times were called for [154].

9.2.4 Hot extraction (HE) methods

Hot extraction based methods were developed for rapid analysis of hydrogen in welds [147, 153, 154]. In these methods, H_D from a weldment is extracted at very high temperatures, $\sim 400^\circ\text{C}$. At such higher temperatures, the collection of H_D is accomplished within 0.5 h and the total time of H_D measurement is less than 1 h. Also, it is found that the H_D contents measured using the hot extraction methods are precise, reproducible, repeatable and are in good agreement with the primary and other alternative standard methods, therefore reliable [154-164]. At present, there are many equipments available for the hot extraction of H_D from weldments. In general, all these equipments have two parts, a hot extraction module for the extraction and collection of hydrogen from the weld specimen at higher temperatures ($\geq 400^\circ\text{C}$) and an analyzer for the detection and analysis of hydrogen extracted. Generally, a quartz tube is used for the hot extraction of diffusible hydrogen from weldments [165]. The commonly used hydrogen detectors are GC and mass spectrometry. Some commonly used hot extraction equipments are shown in **Fig. 24**. Recently an inexpensive and user friendly hot extraction method using a Nafion based proton exchange membrane hydrogen sensor (PEMHS) for hydrogen detection was

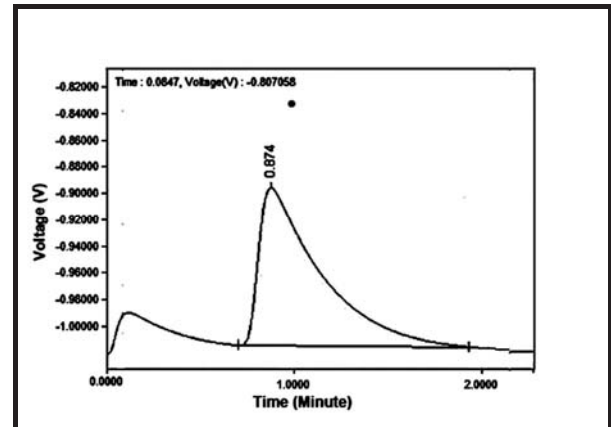


Fig. 23 Response of GC for a hydrogen injection

developed for the rapid determination of H_D . The detailed principle and procedure of H_D measurement using the HE-PEMHS sensor is detailed elsewhere [161-163, 166-168]. However, the two principal objections of using higher temperatures, the potential loss of hydrogen through reactions with oxide layers present on the specimen surface [147, 148] and the risk of residual hydrogen release at higher temperatures remained intact in this method. To remove the surface oxide, full sample cleaning by wire brushing was proposed [155]. The second issue was which would lead to an overestimation of H_D . However, residual hydrogen release up to 400°C was either found to be insignificant or neglected in view of environmental and safety benefits associated with using this method [147, 156]. At present, hot extraction method is in wide use with welding consumable manufacturers. However, the equipments used in the HE method are very expensive and are not easily available. Also, the hot extraction methods are very sophisticated to use. In these methods, the evacuation of the chamber containing the weld specimen takes some time. Therefore, the initial hydrogen loss would be more in the hot extraction method than the other methods operated at lower temperatures. The fact that the H_D content obtained with HE method is a mixture of residual and diffusible hydrogen and is in good agreement with those obtained in the low temperature methods would be leading to an overestimation of the H_D contents in HE methods.

9.2.5 Vacuum-Extraction methods

Two types of vacuum extraction methods are reported in the literature; one measuring hydrogen at room temperatures [148] and the other at high temperatures [11]. Schematics of these two methods are shown in **Fig. 25**. The investigator of room temperature vacuum extraction method claims that the method measures H_D at a better accuracy than glycerin method. In the vacuum hot extraction method, the weld specimen is heated at higher temperatures in a silica furnace tube for extraction of H_D . Hydrogen along with any other gas so extracted is passed through two nitrogen cold traps into an expansion volume where condensable gases freeze out. The combined pressure of hydrogen and other gases reaching

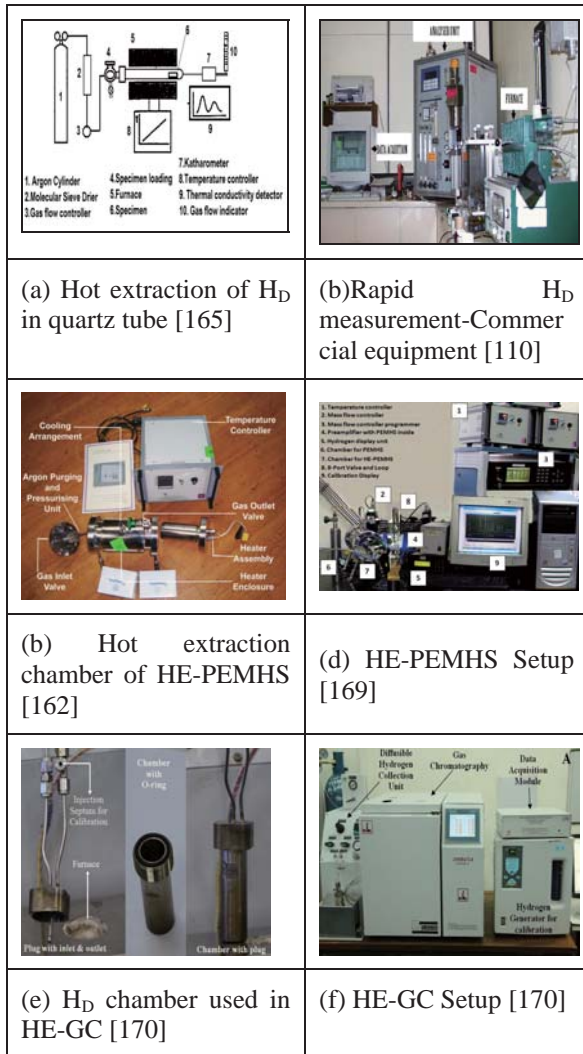


Fig. 24 Different Hot extraction setups for H_D measurement

the expansion volume is monitored by a pressure gauge till the hydrogen evolution ceases. Hydrogen is removed through the palladium/silver osmosis tube and pressure of rest of the gases is measured. The difference in these two pressures is the pressure of H_D . The H_D contents obtained with this method are on the lower side as compared to that using the carrier gas hot extraction method [11].

9.2.6 Other methods for H_D measurement

Apart from the above mentioned methods, there are many other methods which are neither included in any standard nor are in wide practice either because of serious drawbacks or because of limited investigation and availability. Most of these methods are similar to mercury or glycerin methods in principle which is based on volumetric displacement of a liquid/fluid by the diffusible hydrogen evolved from the weld specimen and subsequent volume measurement. These differ only with respect to the type of fluids over which diffusible hydrogen is collected. The liquids which are employed in these methods include silicone oil [171], water [172],

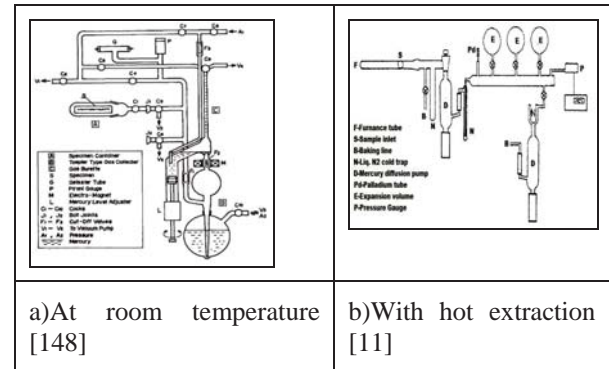


Fig. 25 Vacuum extraction apparatus for diffusible hydrogen measurement

10N K_2CO_3 [150], ethyl alcohol, ethylene glycol, paraffin and carbon tetrachloride [137]. The percentage of diffusible hydrogen collection over these fluids in comparison to mercury is given in **Table 6**.

Except for the collection over mercury, all the other volume displacement methods mentioned above are out-of-date and are not used for H_D measurement because of their poor accuracy. However, the collection over glycerin is still in use following some modifications [140].

9.2.7 Methods for the determination of local hydrogen concentration

The methods discussed in the previous sections, however, are not able to determine the local hydrogen concentration in a specific area of the weld. Only the bulk hydrogen can be measured using these methods. However, it is known that residual stress is localized in some regions of the weld. Therefore, studies on the local HAC susceptibility of a weldment requires the determination of local hydrogen concentrations. For this, Olson et al and Smith have used laser ablation methods which use laser induced breakdown spectroscopy combined either with GC or with Mass spectrometry [149, 165]. Olson et al and Smith also patented another equipment which uses a tungsten oxide based optoelectronic or fiber optic sensor [165, 173, 174] to determine the local hydrogen concentration. The sensor has a hydrogen sensing layer which comprises of the a chemochromic tungsten oxide. The sensing layer undergoes changes in physical properties, such as optical transmission properties, when it reacts With hydrogen. The changes are measured to determine the amount of hydrogen evolving from the sample area A Seebach hydrogen instrument was also developed for the estimation of H_D content in welds based on the measurement of thermoelectric coefficient [165, 175]. Recently, Lasseigne et al [176, 177] have developed a non-contact hydrogen sensor based on low frequency impedance measurement for real time measurement of diffusible hydrogen. However, at present, these methods are not adopted for the diffusible hydrogen measurement in welds.

Table 6 Efficiency of H_D collection over different collecting fluids [137]

Collecting mediums	Efficiency of H_D collection (%)	Remark
Mercury	100	Widely Accepted
‡ 10N K_2CO_3	100	Insufficient investigation
*Water	100	Insufficient investigation
Silicone oil	100‡, 5-32	Insufficient investigation
Glycerin	79-88	Poor accuracy
Ethyl alcohol	23-39	Poor accuracy
Distilled water	58-72	Poor accuracy
Ethylene glycol	18-32	Poor accuracy
Paraffin	10-19	Poor accuracy
Carbon tetrachloride	10-20	Poor accuracy

‡[150], †[171], *[172]

9.3 Comparison of the H_D content obtained with different methods

9.3.1 Glycerin method Vs Mercury method

As it was mentioned in the previous sections, glycerin method produced lower levels of hydrogen as compared to the mercury method. Kotecki [135] has summed up three studies which compared the results of the glycerin and the IIW mercury methods. The correlating relationships obtained are given below.

$$H_{JIS} = 0.64H_{IIW} - 0.93 \dots (22)$$

$$H_{JIS} = 0.67H_{IIW} - 0.80 \dots (23)$$

$$H_{JIS} = 0.79H_{IIW} - 1.73 \dots (24)$$

The above relationships show very little difference. However, it is found that results with glycerin method are consistently lower than those with mercury method.

9.3.2 Mercury method Vs GC method

Hydrogen contents obtained with GC method (H_{GC}) at 150°C showed good correlation against those with the mercury method (H_{IIW}). A correlating relationship reported is given below [139]:

$$H_{GC} = 1.05H_{IIW} \dots (25)$$

9.3.3 Mercury method Vs HE method

Hydrogen contents obtained with hot extraction method (H_{HE}), HE-PEMHS method (H_{PEMHS}) and gas chromatography at 400°C (H_{HE-GC}) showed good correlation with those from the mercury method (H_{IIW}). The correlation obtained from a round robin test is given below [157, 162, 170]:

$$H_{HE} = 0.94H_{IIW} - 0.37 \dots (26)$$

$$H_{PEMHS} = 0.998H_{IIW} + 0.03 \dots (27)$$

$$H_{HE-GC} = 1.005H_{IIW} + 0.22 \dots (28)$$

The hydrogen contents obtained with HE-PEMHS (H_{PEMHS}) are also in good agreement with those obtained with a commercial H_D -Analyzer ($H_{ANALYSER}$) as given below [162]:

$$H_{PEMHS} = 0.99H_{ANALYSER} + 0.03 \dots (29)$$

The H_D contents are determined by static (H_{STATIC}) and dynamic ($H_{DYNAMIC}$) hot extraction measurements on an international round robin test [158]. Dynamic measurements stands for the hot extraction of H_D and measurement at 400°C where as static measurement stands for H_D measurement at lower temperatures. The following correlations are obtained:

$$H_{DYNAMIC} = 1.14H_{STATIC}(45^\circ C) \dots (30)$$

$$H_{DYNAMIC} = 0.78H_{STATIC}(100^\circ C) \dots (31)$$

$$H_{DYNAMIC} = 0.76H_{STATIC}(150^\circ C) \dots (32)$$

The correlations show that the static and dynamic measurements may yield slightly different results depending upon the temperature of the static measurement. Therefore, the hot extraction methods show good accuracy, reproducibility and good correlation with the primary IIW mercury method.

10. Summary

A broad literature review of various aspects of hydrogen in steel weldments is carried out. It is understood that proper knowledge of H_D content is essential to choose appropriate preheat temperatures to avoid the risk of HAC. Measurement of local hydrogen concentration in the weldment would enable a deep understanding on the HAC in the weldments. There is a need to ensure that H_D is controlled in welding consumables and hydrogen is allowed to diffuse out from steel welds before they are cooled to ambient temperatures to prevent cracking. H_D measurement is an important step in achieving this objective. There are many methods available for the measurements of H_D

content in the weldments. Among these, the hot extraction based methods are better than the other low temperature methods with respect to accuracy, reproducibility and pace. However, new techniques are being developed in the pursuit of a method which would enable rapid measurement of the bulk as well as the local hydrogen concentration while being cost-effective, accurate and robust. Also, there is a need for the measurement of local hydrogen concentration in the welds for a better understanding of HAC.

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