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HYDROGEN IN STEEL

A review of the factors affecting
permeation and related problems

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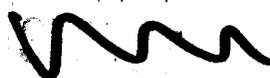
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INTRODUCTION

The effect of hydrogen in steel has been a subject of interest in the Recovery and Reservoir group for some time. Recently an analytical method of extreme sensitivity has been developed for the determination of tritium in stainless steel.* In essence the method provides information relative to the amount and the location of tritium in the sample by determination of the level of radioactivity due to tritium. This method has initiated several research investigations and has been incorporated into the Reservoir Surveillance program.

This report is intended to supply the basic background information that would be useful in performance of the various duties associated with these programs. It is not intended to supply detailed information in any specific area.

Because of inconsistencies with respect to terminology which appears in the literature dealing with the subject of hydrogen in steel, a brief listing of the more important terms and their definitions as used in this report is given below.

* MLM-CF-65-4-535, p. 8



Adsorption: The interaction of the gas phase with the surface of the solid.

Solubility: The ability of the solid to retain the dissolved hydrogen.

Diffusion: The movement of the hydrogen within the body of the solid.

Permeability: The complete process of adsorption, solubility and diffusion.





ADSORPTION AND OTHER SURFACE PHENOMENA

The molecular forces at the surface of a solid are in a state of unsaturation. In order to satisfy this unsaturation these molecules will attract and retain gases with which they may come in contact. This adsorption process can be divided into two phases, Van der Waals or (physical) adsorption and chemical adsorption.

The Van der Waals adsorption is easily established and is found in all instances. The molecular forces involved in the Van der Waals adsorption are very weak and usually have an effective range of less than the diameter of the molecule,² consequently, they cannot form a layer more than a single molecule in depth.¹

Chemical adsorption, at normal temperature, is not a chemical combination but rather an attraction between the metal surface and the gas molecule.¹

The factors affecting the amount of gas adsorbed on the surface are temperature, pressure, surface condition and a constant for a given gas-metal system. The Van der Waals adsorption is directly proportional to pressure, inversely proportional to temperature and is reversible in both instances. Chemical adsorption, however, is



directly proportional to both pressure and temperature; the former may be reversible but never the latter.

The adsorption of molecules in a given gas-metal system at a given pressure and temperature will depend on the rate of condensation and evaporation of the molecules occurring at the gas-metal interface, this rate being controlled by the active surface remaining, i.e., that surface not already covered by molecules. The effect of this is that when the adsorption process first starts the adsorption rate is highest, then falls off as the surface becomes saturated. Mathematically for the condensation rate this becomes:

$$k_1 (1-\theta)P$$

where θ is the fraction of the active surface covered by molecules, P is the Pressure and k_1 is a constant. Then the rate of evaporation would be $k_2 \theta$ where k_2 is the evaporation rate of the fully covered active surface. A state of equilibrium will then exist when:

$$k_1 (1 - \theta) P = k_2 \theta$$

and the fraction of the surface covered by the adsorbed gas would be:

$$k_1 P/k_2 + k_1 P$$

In the above we have assumed that the surface forces are acting on the molecules, if they are in fact, however, acting on the individual



atoms, as is very likely the case,¹ then the molecules that are involved in evaporation may not necessarily be composed of the same atoms that were paired on condensation. This being the case, then individual atoms would be isolated on the surface when atoms from two adjacent molecules evaporated. This being the case the above equation becomes

$$k_1 (1 - \theta)^2 P$$

for condensation and

$$k_2 \theta^2$$

for evaporation and

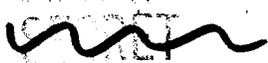
$$k_1 (1 - \theta)^2 P = k_2 \theta^2$$

the state of equilibrium. Thus the adsorbed gas varies with the square roote of the pressure.

The fraction of the surface covered, at equilibrium and normal pressures, is a very small part of the total surface area.² It would require 5.67×10^5 c³ of gas to cover an area of one square centimeter with a monomolecular layer of hydrogen.¹

It is an accepted fact that hydrogen must be in the atomic state in order to be dissolved into steel.² We have described above how a diatomic gas such as hydrogen can be reduced to the atomic state on





the surface of a metal. There are several other ways that atomic hydrogen can be introduced to the surface of a metal such as high pressure disassociation,³ high temperature disassociation,³ reaction with an acid,⁴ electrolysis,⁴ and ionization.⁴

If we define the rate-controlling process for permeation as the slowest step in that process under equilibrium conditions, then whatever mechanism is supplying the atoms to the surface may in the instance of very low pressure or low temperature be the process which determines the permeation rate.⁴





SOLUBILITY

It has been proven by Edwards⁵ that the diffusion of a gas through a metal occurs for the most part through the crystal lattice rather than along grain boundaries. The fact then, that hydrogen will pass through a metal, leads to the reasonable assumption that to some extent it must be soluble in the metal.²

A distinct classification of hydrogen-metal systems may be made. Those systems which are determined to have a negative heat of solution, such as hydrogen-palladium, are considered exothermic systems, while those having a positive heat of solution such as hydrogen-stainless steel, are considered endothermic systems. An important property of the endothermic occluders is that the solubility increases with an increasing temperature.

There are many factors which affect the solubility of hydrogen in steel. The most important of these are pressure, temperature, crystal structure, and alloying materials. The degree of cold working of the metal is another potentially significant factor.

Following is a brief description of the effects which these variables are known to have on the solubility of hydrogen in steel.





Temperature Effect

As stated above the increase in solubility is directly proportional to an increase in temperature. This relationship has been fairly well established in the region above 300°C. The exact relationship is that the log of the solubility is proportional to the negative reciprocal of the absolute temperature.⁶ The relationship at temperatures below 300°C has not been completely established.

Pressure Effect

The relationship of pressure to solubility has been investigated quite extensively for both liquid and solid steel,⁷ and has been found to vary directly as the square root of the pressure for pressure from the micron range⁸ up to all except extreme pressure.⁶

Crystal Structure Effect

Iron exhibits three critical temperatures for the solid, corresponding to phase transformations. At each critical temperature and at the melting point, the solubility of the metal increases. At the alpha-gamma transition and at the melting point the solubility increases considerably.¹ This increase in solubility is believed to be due to the fact that hydrogen can be more readily located in the interstitial sites of the looser face-centered (gamma) structure than in the more close packed body-centered structure.⁹





Alloying Materials Effect

It has been found that the solubility of a iron base alloy may be controlled by the addition of alloying constituents. For instance, nickel exhibits a higher solubility for hydrogen than does iron, while the inverse is true for chromium. Therefore, an alloy of iron-nickel will have a higher hydrogen solubility than an iron chromium alloy and the alloys of iron-nickel-chromium will have a solubility much the same as that for iron.¹

Cold Working Effect

There is no general agreement in the literature that cold working will cause an increase in the hydrogen solubility, however, there are some reported instances of increased solubility due to cold working. This increase in solubility due to cold working is attributed to the existence of traps where hydrogen in excess of the equilibrium lattice solubility is accommodated.⁹

The general equation for describing solubility for diatomic gases is normally written:

$$s = S P e^{-E/2RT}$$

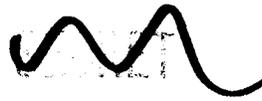
where: s = Solubility in cc of gas/100 grams of metal
S = Solubility constant
P = Gas pressure
R = Gas constant
T = Absolute temperature
E = Activation energy





The activation energy is the heat absorbed in calories/gram mole of hydrogen and can be derived from a linear plot of log of s vs $1/T$ at constant pressure.





DIFFUSION

It was pointed out earlier in this report, in the section dealing with solubility, that hydrogen atoms diffusing in a metal, do so through the crystal lattice, rather than along the grain boundaries. It is, therefore, quite natural to assume that any movement of these atoms, while in solution in the crystal lattice would likewise occur through the crystal lattice.¹⁰ The driving force for this phenomenon is considered to be the hydrogen concentration gradient in existence between the surface and the interior of the solid.³

The diffusion process just described is extremely sensitive with regard to type and thickness of metal, pressure, and temperature. The effects upon the diffusion by these variables will be discussed briefly in the succeeding paragraphs.

Type of Metal

While hydrogen will diffuse in almost all metals, it has been established that it does so at vastly different rates in different metals. Niobium and palladium, for example, have a very high rate of diffusion while molybdenum and tungsten have a very low rate of diffusion.⁴ Intermediate to these two extreme cases, is the rate of diffusion related to iron and iron alloys. It is interesting to





note that, while the rate of hydrogen diffusion in steel will not approach that of niobium or palladium system, it is still many times the rate of any other substance. An iron alloy generally has a lower coefficient of diffusion than does pure iron. For example, the diffusion coefficient for 347 stainless steel at 570°C is only about five per cent that of pure iron at the same temperature.¹¹

Pressure

There is a square root relationship of the pressure to diffusion rate. This relationship is valid in general only at higher pressures, atmosphere and above,¹ while in the low pressure region the relationship becomes more linear.⁸

Mathematically this is expressed for large values of P as

$$R = \alpha \frac{A}{d} P$$

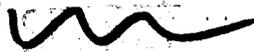
and for small values of P as

$$R = \gamma AP$$

where, R equals the rate of permeation cc/hr/cm², P is the pressure, A is the area in cm², d the thickness in mm, and α and γ are the permeability coefficients.¹¹

Temperature

In general, metals exhibit a negligible rate of diffusion at low temperature which increases rapidly as the temperature increases.



The increase described here is much greater than the increase in solubility which accompanies a rise in temperature. At lower temperatures there is a noticeable tendency for the diffusion curves for various metals to spread out while at higher temperatures they tend to converge.⁸ For example, at 1000°C the permeability of the metals for which data are available, varies by only about a factor of ten while at low temperature the variance may be several orders of magnitude.¹² The diffusion rate for iron is about one thousand times that for type 347 stainless steel at 100°C but only about five times that of stainless steel at 700°C.⁸ This exponential form of temperature dependence on diffusion is brought about by the vibrational excitation of the atoms which expand the lattice and allow gas atoms to move from one interstitial site to another. Only those atoms which possess high energy with respect to average energy of the atoms can make this move, since repulsive forces must be overcome to force the foreign atoms through the energy which bind the metal together.⁴

This exponential form of temperature dependence on the permeability coefficients α and γ can be described mathematically as

$$\alpha = \alpha^0 e^{-E/2R_0T} \quad \text{and}$$
$$\gamma = \gamma^0 e^{-E^1/R_0T}$$



where E is the high pressure activation energy and E^1 is the low pressure activation energy in calories/mole, R_0 is the gas constant and T is the absolute temperature.

Thickness of Material

The thickness of material has only a direct affect on the diffusion of hydrogen through steel so the diffusion of hydrogen cannot be greatly reduced by increasing the thickness.¹² If adsorption is the rate controlling process in permeation then the inverse thickness law cannot be expected to apply. In such a case the thickness would produce less decrease in the rate of permeation than predicted by the inverse thickness law.⁸

The following expression relates the rate of diffusion to the variables just discussed as they affect the diffusion of hydrogen through steel, and serves to illustrate the use of the diffusion and solubility constant as well as the activation energy. If R equals the amount of permeation in cc, then

$$R = \frac{SDA}{d} \left(\sqrt{P_1} - \sqrt{P_2} \right) e^{\frac{-E_0}{R_0 T}} t$$

where S = Solubility constant
D = Diffusion constant
A = Area in square centimeters
d = Thickness in mm
 P_1 & P_2 = Pressure on each surface

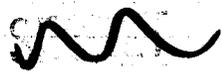




E_0 = Activation energy
 R_0 = Gas constant
 T = Absolute temperature
 t = Time in hours

To summarize we can say that the rate of diffusion of hydrogen through steel will vary -

directly as the area.
directly as the square root of the pressure.
inversely as the thickness.
exponentially as the reciprocal of the absolute temperature.



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OTHER FACTORS AFFECTING PERMEATION

In the preceding pages we have discussed the effect of pressure and temperature on permeation of hydrogen through steel. There are several other factors which can have a considerable effect on the permeation rate. Among these are oxidation and nitriding of the surface, aging, and the alloying elements. The effect of cold working, and crystal structure will be discussed in the following pages under the title of "Deleterious Effects".

Oxidation

If the base metal forms more than one oxide, a stratified layer of oxides will normally form with the highest oxide on the surface and the lowest oxide next to the base metal. For example, in the case of iron or low carbon steel,⁸

outer layer	2% of thickness	Fe ₂ O ₃
middle layer	10-15% of thickness	Fe ₃ O ₄
inner layer	85-90% of thickness	FeO

These oxides as well as the oxides of nickel, are stable to dry hydrogen up to about 700°C. At temperatures exceeding 700°C reduction of the oxide film occurs and at about 980°C the oxide film is almost removed completely. The most effective oxide coating can be obtained by treating the steel with wet hydrogen

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at a temperature of 840°C to 1000°C, however, CO₂, dry air, oxygen and steam are also very effective.⁸

The effect of the oxide coating on the diffusion rate is substantial, an exposure of 347 stainless steel to an oxidizing condition will produce a decrease in permeability of up to several orders of magnitude.¹³ Even very small amounts of oxygen such as a contaminate in hydrogen can cause a gradual decrease in the diffusion rate.⁸

The most probable explanation of the mechanism for the decrease in the rate of permeation due to oxidation is that the oxide forms a partial cover which limits hydrogen ingress to a smaller area of the surface. If a complete barrier film was formed the solubility in the oxide would be constant and the diffusion through this film would be proportional to the diffusion coefficient, which is not the case. If a complete film was formed and the rate of change from surface solution in the oxide layer to permeation was the limiting factor then the thickness of the oxide layer would not be a factor. The permeation rate decreases as oxidation is increased.¹³

Nitriding

Nitride coating 0.005 inch thick has no effect on the permeation rate, however it does appear that the nitride coating will prevent



the oxidizing effect by preventing the water vapor and oxygen from reaching the surface of the steel.⁸

Ageing

The permeation rate of hydrogen through a clean piece of 347 stainless steel will decrease about tenfold from being exposed to dry hydrogen for 100 hours at 620°C. However, this effect can be removed by pickling, which indicates the aging process is a surface effect. If ageing were caused by some change in the body of the metal the permeation rate would be lowered permanently.⁸

Alloying Elements

The permeation rate of an alloy is approximately a weighted average of the permeation rate of the component metals.⁴ In the case of 18-8 chromium nickel steels, the permeation rate is lower than that for iron or cold rolled steel,⁸ this reduced rate in stainless steel can be attributed to the presence of chromium.¹⁴ Small variations in composition have little or no effect on the rate of permeation, unless there is a change of structure or surface conditions.⁸



ISOTOPE EFFECT

The effects of the isotopes of hydrogen on the solubility and the diffusion of hydrogen have not been investigated to any great extent, especially in the case of tritium. The work that has been done is discussed with respect to activation energy solubility and diffusion.

Activation Energy Isotopic Effect

Randall and Salmom report an observed difference in the low pressure activation energy for deuterium and tritium. Their expression is

$$E^1 (H_2) - E^1 (T_2) = 16.858 \times 10^3 - 19.497 \times 10^3 = -2.639 \times 10^3$$

calories/mole. They maintain that this difference should be less by the same amount by which the zero-point energy of H_2 exceeds that for T_2

$E_0 (H_2) - E_0 (T_2) = 6.204 \times 10^3 - 3.608 \times 10^3 = 2.596 \times 10^3$ calories/mole, which is the case. They advance the theory that this greater zero point energy of H_2 should facilitate its dissociation at the metal surface relative to the dissociation of T_2 with the result that the adsorption of H_2 should require less energy than T_2 , and as a result, they therefore contend that the principal difference in the behavior of the two isotopes at low pressure and at the temperatures studied ($570^\circ C$ and $700^\circ C$) should be that due to the difference in zero-point energies.¹¹





There is, however, disagreement between this work and the work reported by Frank, Lee and Williams who have investigated the ratio of the diffusion coefficients of hydrogen and deuterium in a temperature range of 26°C to 86°C. The latter report that there is no systematic variation of the ratio of the diffusion coefficients with temperature and that therefore there is no difference in the activation energies. They believe that the principle difference in the diffusion coefficient for hydrogen and deuterium is the result of the mass effect which does not vary with temperature. The average value which they obtained for D_H/D_D of 1.37 is very close to the square root of the masses 1.414.¹⁵

Isotope Effect on Diffusion and Solubility

As reported above there is disagreement as to the effect of temperature on the diffusion constant ratio of the isotopes, however, there is a difference in the diffusion and solubility due to the isotope effect of hydrogen, deuterium and tritium with the heavier isotopes diffusing slightly more slowly and being slightly less soluble.



THE DELETERIOUS EFFECT OF HYDROGEN IN STEEL

As stated earlier, there are several ways in which hydrogen, as an undesirable contaminate, can enter the crystal lattice of a steel. In general this will occur during any operation which causes a dissociation of the hydrogen molecules, such as an exposure to hydrogen gas or steam at high temperature, pickling operation, corrosion, etc.

The undesirability of hydrogen in steel is a result of its effect on the tensile strength, yield point and the density of the metal. These are relatively insignificant, however, when compared to the embrittlement and cracking which it may produce.

With regard to embrittlement, it may be said that hydrogen atoms located in the interstitial sites will always produce embrittlement¹ of the metal to some extent. This does not mean, however, that it will always produce cracking in the metal.³ For this to occur, the hydrogen must be highly mobile or the metal must be in a state of sustained stress. For example, austenite steel has a higher hydrogen solubility than do ferrite or martensite, but it does not produce the cracking problem they do. This is due to its lower rate of hydrogen diffusion which prohibits the hydrogen from



moving as readily to stressed areas and thus propagating cracks. However, in the presence of a sustained stress above some minimum level hydrogen can cause embrittlement and ultimate cracking in almost any steel.

In the case of a phase transformation to ferrite, or martensite, cold working,⁴ or hardening, the higher rate of diffusion produced will allow any hydrogen present to move more rapidly to areas of stress and accumulate until the concentration is sufficient to propagate a crack. This crack will move slowly as the concentration of hydrogen diffuses to the tip. It is because of this requirement that a crack can only move at a rate determined by the hydrogen diffusion. If a strain rate is too high to allow this diffusion then the hydrogen embrittlement and cracking is not the failure mechanism.

The minimum stress for failure is influenced primarily by the strength level of the steel, with the minimum stress for failure decreasing as the strength level of the steel is increased. The minimum amount of hydrogen required to cause cracking can under the proper conditions be a little 1 ppm average hydrogen content.³





CONCLUSION

While the permeation of hydrogen through steel and the accompanying effects upon the metal have been the subject of considerable research effort, the information thus obtained has been somewhat limited in certain areas. In particular, it has dealt with relatively high permeation rates only, using thin specimens at high temperature and normal hydrogen exposure. Unfortunately, little information has been derived concerning thick specimens at lower temperatures and high pressure. Likewise there has been little correlation of the effect due to the isotopes of hydrogen.

Almost all of the techniques used to collect data have been some variation of a volume measurement of the hydrogen gas after it had been passed through a membrane. The natural advantage of the counting techniques that can be used with tritium and the inherent sensitivity of this method has not as yet been put to extensive use.


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