UNAPPROVED

PRACTICAL APPLICATIONS OF HYDROGEN PERMEATION MONITORING

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ABSTRACT

Practical applications of hydrogen permeation monitoring and modeling are presented. Applications discussed are effectiveness of HVOF metalizing on preventing permeation and monitoring sulfide scale stability. Use of a simple modeling program to determine a diffusion coefficient for seamless pipe during full ring testing and to determine sample soak duration when running hydrogen charged mechanical tests will be presented.

Key Words: Hydrogen, Permeation, Hydrogen Permeation, Steel, Diffusion, Sulfide Stress Cracking, Hydrogen Embrittlement, Sour Service, Sour Service Testing, Fracture Mechanics, Amine, Flash Drum, Blistering, DCB, Full Ring Test

INTRODUCTION

The impact of hydrogen on steel is important to the oil industry because steel is the most widely used material of construction. When steel absorbs hydrogen, its properties can change, and in some cases lead to cracking and failure. Applications where absorption of hydrogen by steel occurs are services containing H_2S , HF or where cathodic protection is present, or by molecular hydrogen from acid corrosion at elevated temperatures. Additional issues arise in the very high strength steels where simple atmospheric exposure can result in sufficient hydrogen charging to cause cracking.

Such a pervasive issue as hydrogen affects on steel should be well understood since there are so many practical applications where safe operation depends upon such

understanding. Indeed there are industry rules for services known to cause cracking such as H_2S and HF. The most well known are the limits set forth in NACE MR0175 and ISO 15156 for sour services. The imposed limits add to construction costs so there is incentive to make sure they are applied appropriately and only where needed. Despite this incentive, there are several aspects of hydrogen effects that are not well understood.

Simply predicting sour service environments that will be particularly harsh is not well understood. The role of H_2S in aqueous solution is a variable of its concentration, temperature, pressure, solution pH, oxygen concentration, velocity and the other ionic species present in the solution. In many practical applications, these variables are not constant and indeed continuously change. Additional complexity arises in the corrosion process itself because corrosion by-product films can moderate the corrosion reaction rate. When services contain both water and oil, the oil also interacts with the surface and can retard the corrosion rate.

The steel itself interacts in the corrosion process and hydrogen charging effects can be altered by compositional and/or microstructural variations in the steel, not to mention welds. This is particularly true at low (i.e. ambient) temperatures where hydrogen segregation at grain boundaries and inclusions is more pronounced. Finally the strength of the steel and the state of stress in the steel can affect hydrogen mobility which in turn then causes changes in the steels ability to withstand stress without cracking.

The many variables that affect hydrogen charging in steel remains one of the most active areas of research in the oil industry. Measuring and modeling hydrogen charging is one such active area and is the primary subject of this paper. If one could easily monitor actual equipment for actual hydrogen charging, much of the theoretical guesswork would be unnecessary.

Until recently, such field measurements were limited in practicality because they were typically neither real time nor portable, nor particularly durable. The introduction of the Hydrosteel monitor by Ion Science¹ has partially solved these limitations. Use of this monitor both in the field and in the lab has lead to a deeper understanding of the process whereby hydrogen is absorbed into steel.

HYDROGEN BLISTERING CASE HISTORY

An acid gas plant rich amine flash drum suffered severe hydrogen blistering. The damage was extensive and major repairs were necessary to restore the vessel to a reliable condition. Some blisters evaluated as insignificant were left in place and would be monitored to assure they remained insignificant. To prevent reoccurrence of blistering, the vessel was internally coated using a metalspray process. The metalspray process places a thin layer of corrosion resistant alloy (CRA) on top of the carbon steel in hopes of preventing the sour amine from interacting with the steal.

¹ Hydrosteel permeation technology, Ion Science Ltd, UK

Subsequent external UT monitoring of the remaining blisters found a pattern of slow growth in size, after startup. This trend continued for several months before slowing down. The growth was such that it was more than could be explained by measurement errors yet not enough to cause any threat to vessel integrity. However, the cause was not understood and there was concern about the metalspray perhaps failing and coming off.

To check for this, the hydrogen permeation tool was used to see if hydrogen was still permeating through the steel. No significant hydrogen was detected. At the time it was postulated that perhaps the blister itself absorbed the hydrogen and prevented it from going through to the outside surface. Another theory was that porosity in the metalspray coating may be letting a small amount of the rich amine interact with the steel surface, thereby generating a small amount of hydrogen. Still a third theory postulated the hydrogen in the blister was still interacting with the steel and no new hydrogen was needed for this to occur.

To evaluate the situation, an opportunity arose whereby the metalspray coating could be tested under laboratory conditions as part of a joint industrial project ^{(1).} These trials engaged two 16mm thick steel plates, simultaneously exposed to 26 litres of standard NACE TM0284 solution for 14 days. Two hydrogen permeation tools continuously monitored hydrogen exit from the plates during trials, and daily measurements of corrosion rate and crack incidence were monitored. The apparatus is shown in Figure 1.

The first experiments investigated if blistering altered the pattern of hydrogen permeation by engaging one plate known to suffer HIC (plate B) and a second plate known to be resistant to HIC (Plate A). NACE TM0284 A (buffered pH 2.7) was used. No metalizing was present on the steel plates. From both plates, hydrogen permeation was monitored and trended for 14 days. Plate B developed HIC cracking blisters as expected and Plate A did not, also as expected. Figure 2 shows the trend of measured hydrogen that permeated through Plates A & B. The permeation data shows similar trends for both plates, with slightly higher permeation rates going through Plate B. Note that the buffered solution results in a quick rise in permeation that then remains relatively constant. While corrosion products formed, they did not result in a decrease in the generation of hydrogen at the exposed surface.

The next experiment was set up identically with the exception that two Plate B's were used. One Plate B was metalized using the same installer and coating system as used in the rich amine flash drum. Results from permeation monitoring during the test are shown in Figure 3. Figure 4 shows a magnified cross section of the metalized layer after the test. Plate B without metalizing showed a permeation trend very similar to as in the first test, and HIC cracked again as expected. Plat B with metalspray showed no permeation and did not HIC crack. Note that previous trials and careful plate sourcing and preparation verified consistent hydrogen induced cracking (HIC) of plate B steel in the absence of metal spray.

⁽¹⁾ Fluxhicor Joint Industry Project, Bodycote Materials Testing, UK, Ion Science Ltd, UK

Conclusions From These Experiments Are: ROVED

- If a plate is blistering, the rate and pattern of hydrogen permeation on the outside surface may not provide any indication of the blistering process. Permeation rate seems independent of blistering which is counterintuitive because some of the hydrogen must be trapped in the blisters. The amount of hydrogen needed to cause blisters of the size formed in these experiments was not sufficient to significantly alter the permeation rate at the OD surface.
- A CRA metalspray coating of the type used in the rich amine flash drum provides a good barrier to prevent interaction of the corrosive environment with the steel substrate.
- For at least one specific plate, a rate of hydrogen permeation/activity to cause HIC was determined.

PREDICTING PERMEATION

Assuring materials of construction are safe in sour service is done by testing, once one starts using high strength materials rather than annealed or normalized grades. Sour service testing is guided by several industry specifications like NACE TM0177, NACE TM0284 and ISO15156. These tests place material samples of various sizes and shapes in various standardized sour solutions to determine if they are acceptable or not, or like the DCB test, derive fracture arrest stress intensity values. The degree to which hydrogen charging occurs and when in time are not required parameters to monitor in these tests. As a result, there is ongoing controversy about the relative severity of various test solutions and the impact of specimen size and test temperature on test results.

To help address these concerns, one of the authors commissioned another of the authors to develop a simple Excel based spreadsheet that would perform the necessary calculations to determine how size, temperature and exposure modality (one sided vs two sided exposure and plate vs pipe) interact as a function of time during a test. The model is based on application of Fick's diffusion law, assuming zero hydrogen at the exit face at all times, and a concentration and steel depth independent D value, and no allowance for hydrogen accumulation in voids or permanent traps. Variable parameters were steel thickness, cylindricality, temperature, and the variation of surface hydrogen entry concentration with time, needed to calculate hydrogen concentrations and flux emanating from steel over a time period of interest.

Among the first issues that has to be resolved in such a model is what diffusion coefficient should be used for steel. Many researchers have concluded there is a significant range for the value of the diffusion coefficient for typical carbon steels.

Diffusion coefficients of steel are low as compared with values obtained for pure iron, especially at low temperatures. The relationship for a comprehensive range of commercial and synthetic steels is addressed by Grabke and Reicke ¹, who adopt the theoretical approach to hydrogen diffusion of McNabb *et al.*², based on the density of

deep and 'flat' traps in steel, and hydrogen binding energies. For pure iron, the temperature dependent diffusion coefficient is found to be given by:

 $D_{\rm H} = (5.12 + 0.6) \cdot 10^{-4} \exp[-(4.15 + 0.03) / \text{RT}]$ (1)

For all other steels,

$$\begin{split} D_{eff} &= D_{H} / (1 + \alpha) \text{ where} \\ \alpha &= (N_{ft} / N) \exp (\Delta S_{ft}^{0} / R) \exp (\Delta H_{ft}^{0} / RT) \\ Nft &= \text{concentration of flat traps} \\ N &= \text{number of normal interstitial sites} \\ \Delta S_{ft}^{0} \text{ is the hydrogen flat trap binding entropy} \\ \Delta H_{ft}^{0} \text{ is the hydrogen flat trap binding enthalpy} \end{split}$$

Grabke and Riecke present experimental data for both commercial and synthetic steels which conforms to equation (2), and the corresponding flat trap densities and energies are tabulated.

(2)

In the flux modeling program, equation (2) was adopted, using, in this work, appropriate values for a quench and tempered 'commercial pipeline steel' ('St 0': C 0.05, Si 0.45, Mn 1.45, P 0.0009, S 0.001, Mo 0.007, Ni 0.23, Cr 0.3, V 0.035, Nb 0.047)

In one set of experiments, a quench and tempered API 5L Grade X60 heavy wall pipe was subjected to still another sour service test called the Full Ring Test. In this test, a complete pipe is mechanically loaded to simulate service loading and is then filled with a sour solution and allowed to sit for 30 days. At the end of the test, the pipe is examined to see if cracks developed in the locations of high stress. The X60 pipe in this test was further subjected to hydrogen permeation monitoring during the test using the hydrogen permeation monitoring during the test using the hydrogen delay before hydrogen made its way from the ID to OD, then a peak rate followed by a decline in permeation.

The flux modeling program was then used to attempt to model the actual results. After some trials, a diffusion coefficient and C_o were found that match the time delay, rate of increase and the peak value reached, assuming a step increase in hydrogen entry concentration. See Figure 6. In reality, corrosion films form and solution pH changes during the test. To model the decline in permeation shown in the experiment, an additional user defined value factor (τ) was used to specify a rate of exponential decrease in hydrogen concentration at the exposed surface. This factor represents how the hydrogen activity at the exposed surface decreases with time. Efforts to date have used a constant value for τ for simplicity, though τ is known to vary according, for example, to the rate at which corrosion products form on steel surfaces.

FRACTURE TOUGHNESS TESTING STEEL EXPOSED TO SOUR SOLUTIONS

Consider a specimen made from 20 mm plate, that will be tested after pre-charging with hydrogen or tested while in solution. In the first case, a primary question is how long to pre-charge the specimen before testing. Using the spreadsheet model, one can easily estimate that peak charging in the center occurs roughly 30 hours after start of immersion at 24°C. See Figure 7. In this case, the sour solution was assumed to be that of one that generates a permeation curve as in Figure 5. An initial hydrogen activity at the exposed surface of 1.65 ppm is assumed. This solution caused a peak concentration and then declined with time. If a solution as in Figure 1 is used (e.g. no decay in hydrogen charging rate at the exposed surfaces), 90% of peak concentration is reached after 90 hours and it is both a higher absolute rate and remains high over time. See Figure 8.

The model can also estimate what will happen if the test temperature is lowered to 7°C instead of a normal test temperature of 24°C. See Figure 9. In this case the peak hydrogen level in the center is not reached for about 45hours. Similarly one can change thickness from 20 mm to 50 mm and see how much longer it takes to reach peak charging. Figure 10 is for a 50 mm wall sample at 24°C. Peak charging is not reached until after several hundred hours.

HYDROGEN ACTIVITY

Measured flux data are often more useful upon conversion to an index relating to hydrogen embrittling. The use of hydrogen activities, in units of bar molecular hydrogen, is advocated in a recent paper by one co-author ⁽³⁾. The conversion of hydrogen flux, temperature and steel thickness to activity is valid as long as a steady state flux of hydrogen through the steel is established. Clearly this assumption becomes increasingly unreliable for colder and increasingly thick-walled equipment, for which steady state permeation can take days to establish.

A specific advantage of the conversion is that activity (as opposed to concentration) of hydrogen in steel is calculable from flux data by reference to permeability (as opposed to diffusivity), which unlike diffusivity, does not vary widely for low temperature steel. Moreover, activities provide an immediately realizable index in terms of crack susceptibility with activities of 500,000 bar from low temperature steel not being uncommon. As a simple example, assume a flux of 500 pl/sqcm/s (picoliters per square centimeter per second) is measured on two different pressure vessels. One vessel is at 30°C and is 25 mm wall. The other vessel is at 50°C and is 7.5 mm wall. One can determine that the lower temperature vessel has a more severe environment by calculating that hydrogen activity on its inside wall is about seven times more aggressive than the warmer vessel. One would predict a significantly higher chance of hydrogen damage in the cooler vessel even though the measured flux is the same between the two vessels.

Conclusions From These Model Cases Are: ROVED

- The nature of the selected sour solution must be understood. If the hydrogen activity decreases with time, peak hydrogen charging is a narrow window in time such that testing much after this point may not be representative of actual worst case conditions.
- If the nature of the solution is such that hydrogen activity remains constant, then a peak concentration is reached and held, such that mechanical tests should respond similarly as long they occur after peak charging has been reached.
- Both temperature and wall thickness can cause a significant change in the time it takes to reach peak charging. If a mechanical test is to be performed, over the time scale at which the load is changing, the loading could interact with the rate of hydrogen charging. An understanding of the interaction between mechanical testing and hydrogen permeation modeling can result in more controlled and consistent testing process.
- Field monitoring of hydrogen permeation must consider wall thickness and temperature to determine severity of the service. The flux rate by itself is at best a crude indicator and may lead an investigator to an incorrect conclusion. Hydrogen activity is a better indicator.

SUMMARY

Progress is being made in understanding how to monitor, predict and model hydrogen charging of steel. New monitoring techniques and simplified modeling tools are combining to provide answers where none existed before. This is important because hydrogen effects on steel are wide spread and still today are a significant source of cracking problems and inspection costs to the oil industry.

Many questions remain unanswered with respect to specific environments that cause hydrogen charging, the magnitude of the charging, how the rate of charging changes with time and how these interact with the loading condition to result in cracking. Another set of unanswered questions revolve around steel making and the factors that make one steel susceptible to cracking while another is resistant. Answering these questions will be aided by having a sound modeling foundation for hydrogen permeation and the ability to easily monitor charging in real time.

REFERENCES

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Figure 1. Apparatus for dual plate charging, as described in the text. The hydrogen permeation tool, engaged to one plate, is shown.



Figure 2 Hydrogen permeation monitoring in NACE TM0284 Solution B (Buffered 2.7 pH) One cannot tell from the trend that Plate B blisters while Plate A does not.



Figure 3 Repeat of the above experiment using two Plate B samples, one of which has been coated by a CRA metalizing spray.



Figure 4 Magnified view in cross section of the CRA metalspray layer after testing. The metalspray layer is unaffected by the exposure.



Figure 5 Hydrogen Permeation Monitoring during a Full Ring Test of Heavy Wall X60 Q&T pipe.



Full Ring Test Hydrogen Permation Modeled

Figure 6 Spreadsheet model of hydrogen permeation matching reality of the full ring test shown in Figure 5



Figure 7 Spreadsheet model of two sided charging of a 20mm wall plate at 24C with decay constant. Time to peak charging of the center section is about 30hrs and then declines to low values over the cross section after about 100hrs.



Figure 8 Same model as in Figure 7 except no decay constant is used. Peak charging still occurs in about 30hrs but at a higher concentration and the through thickness concentration remains at this level over time.



Figure 9 Same conditions as in Figure 8 except temperature is lowered to 7C. Time to peak charging increases to little more than twice as long than at 24C.



Figure 10 Same conditions as in Figure 8 except thickness is increased to 50mm. Time to peak charging increases to about 160hrs vs 30hrs when the wall was 20mm.