Hydrogen-induced cracking and blistering

Hydrogen damage to steel is a well-known consequence of corrosion in sour service. A corrosion inhibitor program can reduce hydrogen entry into the metal. This decreases or eliminates hydrogen damage, resulting in higher profitability and plant availability

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Corrosion costs billions of dollars worldwide. Corrosion damage may lead to a drop in production, the expense of replacing equipment, maintenance and repairs costs, safety hazards or environmental pollution.

If corrosion is slow and well identified, costs can be controlled, as end of life is predictable. Equipment replacement or rehabilitation can be planned and orchestrated years in advance, to cause minimum disruption to the normal, efficient running of the plant. Correspondingly, unanticipated corrosion costs are often compounded by a lack of immediately available services and materials needed for equipment rehabilitation and unplanned upsets, both upstream and downstream of the severe corrosion event. Hydrogen induced cracking (HIC) and the blistering of carbon steel are both such unexpected corrosion phenomenon.

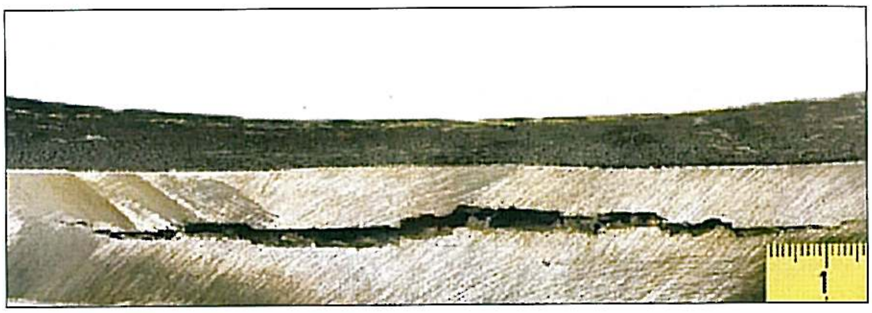

Figure 1 Hydrogen damage

Hydrogen damage (Figure 1) is encountered in many steel processes, such as pickling, electroplating and welding. One essential contributing feature of hydrogen damage to welds is that mobile hydrogen, by virtue of its very increased solubility and diffusivity through steel at elevated temperatures, is generated at a relatively high concentration in certain regions of the weldment (the heat affected zone). As the weldment cools, the solubility decreases, and so the activity of this mobile hydrogen increases.

However, HIC during steel service does not normally involve the cooling of steel after exposure to hydrogen at high temperatures. Usually, active, aqueous acid corrosion by hydrogen promoters — the weak acid hydrides of P, As, Sb, S, Se, Te and F — causes atomic hydrogen to enter the steel at extremely high activities. For instance, the Grabke and Reicke[1] report promoted mobile hydrogen concentration levels in steels at activities of over 1000 bar$^{1/2}$. That is to say, the gaseous hydrogen pressure required to generate the hydrogen in steel concentrations generated by promoters would need to be over one million bar. No wonder steel can be susceptible to hydrogen cracking. The most important hydrogen promoter industrially, and probably the most vigorous,[2] is H_2S, sour gas.

With regards to sour corrosion, the rate of hydrogen entry into the subsurface of a steel subject to sour corrosion is now well known to vary as $[H_2S]^{0.2}$ to $[H_2S]^{0.25}$ (ie, only weakly with sour gas concentration[3-6]). It appears the promoter acts catalytically in favouring the entry of atomic hydrogen into the steel. By contrast, in acid corrosion by non-promoters, such as HCl,[7] cathodically formed atomic hydrogen associates to form molecular hydrogen, which desorbs to be carried off into the process stream as hydrogen gas.

Hydrogen entry is not known to occur through the sulphide scale that frequently results from sour corrosion. Indeed, the passivation of sour corrosion by a variety of sulphide scales that form on carbon steel are a major reason why sour corrosion is not more prolific. Also, sour corrosion can be successfully controlled by inhibitors.

> "Unanticipated corrosion costs are often compounded by a lack of immediately available services and materials needed for equipment rehabilitation and unplanned upsets"

In the absence of inhibitors, hydrogen damage is contingent on the scale being removed due to:

— Dissolution at a pH below about 3–5 (depending on steel surface chemistry[8])

— Oxidation of sulphide scale; for example, during internal inspection, followed by removal of the more soluble iron oxide product

— Erosion corrosion

— At a high pH by complexation of sulphide to form soluble thiocyanide, $Fe(SCN)_4^{2-}$. It is doubtful that cyanide is a promoter itself. It only acts to expose steel to sour gas at a high pH.

Steel's susceptibility to HIC depends upon hydrogen entering the steel at a certain activity and migrating through it. Migrating hydrogen atoms may encounter non-metallic inclusions at the steel centre line and lattice defects, where they segregate and recombine to form molecular hydrogen. Eventually, sufficient pressure forms inside a micro-crack for it to propagate, forming a hydrogen-induced crack discernable by ultrasonic testing. The cracks normally run parallel to the steel surface, which is, therefore, the favoured direction of stress propagation. Apart from the presence of sulphides such as MnS, steel's susceptibility to cracking is influenced by the banding of grains, also running parallel to the surface.

As cracks elongate and join up, the hydrogen activity required to propagate them further decreases, and eventually the metal will deform to produce a discernable blister on the steel's exterior. Such large blisters should not be confused with fish eye-type blisters forming near the surface of relatively soft carbon steels subject to, say, sour gas corrosion.

HIC is observed in steels with high tensile strength, which may be high-carbon steels or non-stainless alloy steels. Another variant of hydrogen-related corrosive damage — sulphide stress corrosion cracking — affects high-strength steels, in which hydrogen migrates to a crack formed on the steel's surface.

HIC may occasionally be delayed beyond the normal timescale of a few hours to a day, to allow for the diffusive migration of hydrogen into and, if not trapped, out of the steel. A high hydrogen entry activity is required, but, in addition, the affected steel is subject to high internal or external stress. Signs of a need for delayed HIC are notches on the work piece's surface or its interior, where hydrogen has concentrated in elastically widened lattice areas.

Hydrogen-induced damage can reveal fracture surfaces that cannot be easily distinguished from cleavage fractures. Intergranular cleavage fractures are often difficult to distinguish from cracks that have been formed by intergranular stress corrosion cracking. In addition, there is the possibility of confusion with intergranular fatigue cracks or intergranular hot cracks.

Corrosion measurement and control

Low carbon and low alloy steels are the preferred materials for most pipes and vessels in the oil industry. Typically, corrosion rates are quoted in units of mm/year or mils/year wall loss, a severe corrosion rate being 1 mm/yr or 40 mil/yr. Corrosion measurement is crucial at all stages of oil production and refining. The most direct measurement of corrosion rate is wall thickness loss, determined by ultrasonic thickness (UT) testing. These small handheld instruments measure the back wall echoes to determine the thickness of the metal.

More accurate thickness measurement is often provided by the field signature method (FSM) and pulsed eddy current (PEC) tools. Both techniques are non-intrusive but fixed methods. They provide information on metal loss over several days. FSM is designed for monitoring corrosion, erosion and cracks in piping systems. This method demonstrates a high sensitivity and accuracy, to measure the metal loss in a piping system. Sensing pins or electrodes are fixed in an array over the monitored area. The typical distance between the sensing pins is two to three times the wall thickness. Detected changes in the electrical field pattern provide information on the corrosion mechanism.

Conventional eddy current methods use single-frequency sinusoidal excitation and give a response as impedance or voltage changes. The PEC technique uses a step function voltage to excite the probe. The advantage of the step function voltage is that it contains a continuum of frequencies. The currents are detected by a receiving probe. The frequency content of the pulses depends on their lengths. The pulse obtained by the receiving probe can be displayed in the form of the variation of amplitude with frequency. The speed of the waves is a function of the frequency. The height of the peak and its time delay is related to the metal thickness.

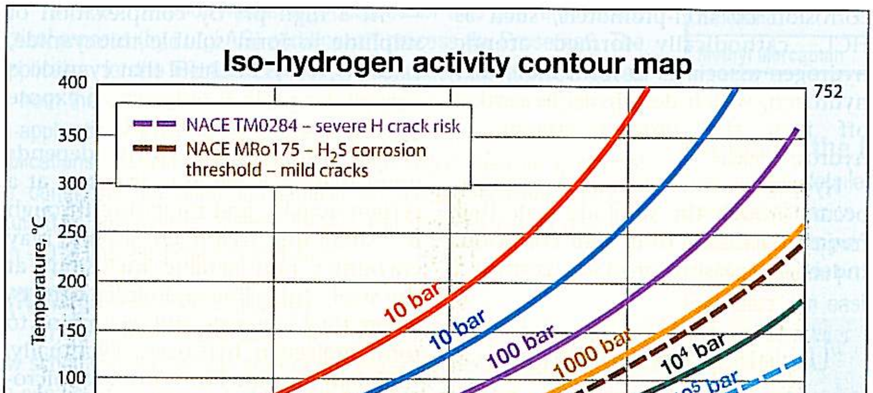

Figure 2 A mapping of hydrogen activities. The activity can be determined from steady-state flux thickness and steel temperature. The values are established from permeability vs temperature data from reference 1

Electrical resistance (ER) probes use the simple principle of an increase in electrical resistance, produced by a decrease in the thickness of a metallic conductor. The increase in electrical resistance of the corroding sensor is measured in comparison to an uncorroded reference element. The sensors do not respond rapidly to a change in corrosive conditions. By decreasing the element thickness, the sensitivity can be improved, resulting in a reduced sensor life. These tools are intrusive and a probe is installed into the pipe or vessel to measure the corrosivity of the process stream directly. Carbonaceous materials or conductive deposits like iron sulphide can distort the readings. Electrical resistance probes do not distinguish between general and localised corrosion forms.

These corrosion-monitoring tools give a good indication of corrosive scenarios that result in wall thickness loss. They do not provide an indication of hydrogen entry severity (ie, of the susceptibility of a scenario to cause HIC). HIC is often not evident as metal wall losses.

Hydrogen flux measurement

An elegant means of determining hydrogen entry is to measure the hydrogen flux exiting a steel surface. After the time required for hydrogen diffusion, and possibly for the infilling of empty hydrogen traps in the steel, this flux corresponds exactly with the previously described hydrogen entry flux accompanying sour corrosion. The flux is defined as a flow of hydrogen per unit across a cross-sectional area of steel surface, with the most common measurement units being pL/cm^2/s. (A number of measurement units for flux have been used over the years, according to measurement techniques and applications. 1 pL refers to 10^{-12} L molecular hydrogen at 1 bar and 20°C. 1 pL/cm^2/s = 0.0079 µA/cm^2 = 4.1 10^{-14} mol H_2/cm^2/s = 8.2 10^{-14} mol H/cm^2/s = 9.3 10–10 Ncm^3/cm^{-2}/s^{-1}.)

Hydrogen only permeates through metals as atomic hydrogen, H. It continues to exist as atomic hydrogen until it arrives at an interface such as a blister, void or crack. Atomic hydrogen arrives more commonly at the external surface of a pipe or vessel, where molecular hydrogen, H_2, is formed and may desorb.

Like the previously described methods, hydrogen flux measurement can be completely non-invasive. However, it differs from the previously described measurements in that they provide a measure of corrosive wall loss averaged over the timescale between two spot measurements. A single spot hydrogen flux measurement provides an indication of corrosion that has been recently active. Of course, a steady-state flux response to a corrosive scenario is only reached after the time required for hydrogen-diffusive processes to equilibrate. Typically, this time delay is an hour to a day, and is slower for thicker, colder steel.

At low temperatures, the correlation between hydrogen flux and corrosion may be complicated by the prospect of not just the hydrogen promoter, typically sour gas, but also other corrodants. However, a steady-state flux, J_{ss}, directly relates to the propensity of corrosive action to cause hydrogen damage. The flux relates to the permeability of steel, P, (hydrogen permeability P though a steel is equal to the product D.S, where S is the hydrogen solubility and D the hydrogen diffusivity. A good source of reference for non-austenitic steel P values derived from D and S data is Grabke and Reicke.[1] These P values increase rapidly with increasing steel temperature T, but surprisingly little with non-metal content, decreases in D caused thereby being offset by increases in solubility, whereby the product D.S is unchanged), thickness, w, and activity at the corroding interface, a_0, expressed in units of (molecular hydrogen pressure)$^{1/2}$, according to :

$$J_{ss} .w = P\, a_0 \qquad (1)$$

It can be seen from equation 1 that if activity a_0 due to a particular corrosion scenario is constant, flux should decrease inversely with thickness. This has been found to be true, at least for thicknesses of steel exceeding 3.0 mm, subject to sour solutions,[9] rearranging equation 1 to:

$$(a_0)^2 = (J_{ss} .w)^2 / P^2 \qquad (2)$$

So, it is reasonable to consider the propensity for corrosion to cause cracking expressed as hydrogen activity in bar equivalent to molecular hydrogen, $(a_0)^2$, to vary as the square of flux multiplied thickness or "flux thickness", in units of pL/cm^2/s x cm, or pL/cm/s. Figure 2 illustrates how hydrogen activity expressed in bar, $(a_0)^2$, varies with flux thickness and temperature.

It is unusual for flux thickness to exceed a few 1000s of pL/cm/s. For example, the severe HIC propensity of NACE test method TM0284, comprising steel exposure to NACE A solution saturated with 1 bar sour gas, generates a flux of about 1600 pL/cm^2/s at 20°C through 1.0 cm-thick A516 steel.[10] The activity is calculated to be about 1.6 x 106 bar hydrogen equivalent.[1] This activity threshold is plotted in Figure 2. It can also be seen that above about 100°C, the crack risk presented by a few 1000s of pL/cm/s is deemed to be mild. Incidents of steel cracking at temperatures above 100°C are rare.

Figure 3 Flux measurement

If the steel is able to sustain severe sour corrosion without significantly trapping the hydrogen, the activity through the steel may be expected to decrease steadily from a^0 at the entry face to approximately zero on the exit face. However, for extensive cracking or blistering, the same severe hydrogen activity will drop to a few bar within the steel. The hydrogen exiting will never exceed a few 10s of pL/cm^2/s.[11] On a microscopic scale, crack initiation requires lower hydrogen activities than crack propagation. On testing hydrogen flux, it is advisable to test near, but not on, a hydrogen blister.

A number of flux measurement technologies have been developed over the years. The technique used in this work has been described as the hydrogen collection method,[12] embodied within a commercial tool, the Hydrosteel 6000 from Ion Science in the UK. The apparatus, depicted in Figure 3, gives reliable hydrogen flux spot readings within minutes of magnetic attachment of a hydrogen collector to a target steel surface. When so engaged, a pump in the handheld instrument causes a flow F of ambient air to be drawn across the effective area A of contact between the collector and test surface into a central capillary through a conduit connecting the collector to the instrument, and across a proprietary amperometric hydrogen sensor within the instrument, where the increase in hydrogen concentration in the air c is registered and converted into a flux according to $J = Fc./A.$[12] The commercial tool provides flux resolution to 1 pL/cm^2/s.

Measurements can be taken with a single probe from small pipes and large vessels, at any orientation and at any temperature up to 500°C (932°F). The instrumentation is intrinsically safe, simple to use and its application requires minimal test surface preparation.

Control of hydrogen damage

Cathodic HIC and blistering are mainly observed in unalloyed and low-alloy ferritic and martensitic steels. There are a number of possible approaches to reduce hydrogen damage. A very expensive solution is to upgrade to higher steel qualities, which are more resistant to hydrogen damage. During metal production, the critical operations for the entry of hydrogen are melting, casting, forging, rolling, welding and electroplating. Optimised manufacturing methods help to reduce the potential for corrosion.

Figure 4 *Cliffy notches and holes on the surface*

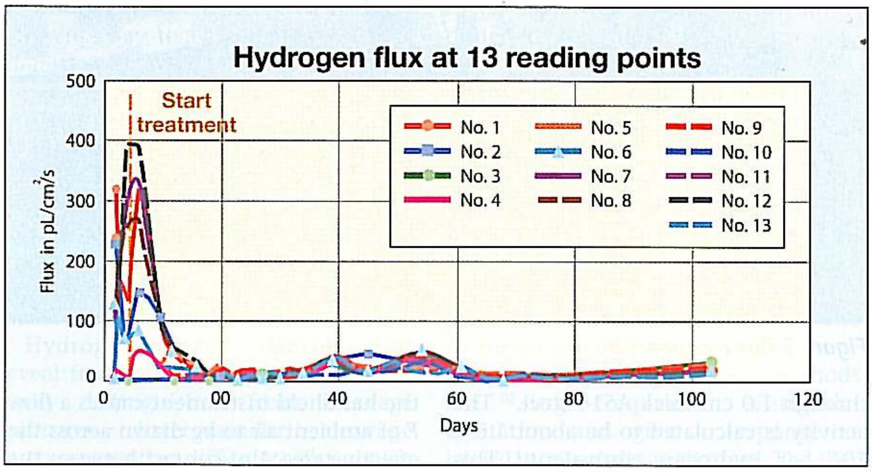

Figure 5 *Hydrogen flux readings*

The best method of controlling hydrogen damage is to limit the contact hydrogen has with the metal. At ambient temperature, materials are most severely jeopardised by hydrogen embrittlement. Unalloyed and low-alloy steels are decarburised with the formation of methane and, later on, blisters between 200 and 500°C. Below 360°C, powerful corrosion inhibitors such as Kurita CI-6302 can be used to significantly reduce the potential for corrosion. The film forming inhibitor is adsorbed into the metal through its polar group. The non-polar tail of the corrosion inhibitor molecule is oriented vertical to the metal surface. The atomic hydrogen reacts with the corrosion inhibitor, which forms a barrier to the metal surface.

Case study

The soot-wash column K-151 at Evonik Oxeno in Marl, Germany was shut down and inspected due to distinctive features. Significant corrosion damage effects were observed on the trays and inner surface of the column. Work pieces of the damaged parts were taken away and analysed in the laboratory for materials testing.

Based on the failure mode, these observations were reported:

— At the cut surface, the metal was cracked parallel to the metal surface

— The metal surface "partially' contained bulges (bubbles)

— Many work pieces showed cliffy notches (Figure 4)

— Some work pieces showed holes, which had a cavity below the interior surface

— Some works pieces showed a considerable decrease in the metal thickness.

Metallographic analysis, scanning electron micrograph (SEM) and infrared spectroscopy (IR) were undertaken. Based on the inspection of the soot-wash column K-151 and analysis of the work pieces, the corrosion mechanism was categorised as hydrogen damage, mainly caused by HIC. The damaged soot-wash column K-151 was replaced and production restarted with a second soot-wash column K-201.

> "Hydrogen damage can occur very fast, so a quick, reliable and accurate indicator of the propensity for hydrogen damage is essential"

To avoid further hydrogen damage, a three-month trial was started after determination of the hydrogen flux baseline data. The selected corrosion inhibitor Kurita CI-6302 was dosed into the system. This product is a powerful, concentrated formulation of film-forming components. It is specifically designed to work in systems with high water-to-hydrocarbon ratios. Typical application areas are systems, where corrosion is initiated by the absorption of hydrogen, acidic or alkaline solutions, hydrogen sulphide or cyanides.

To check the efficiency of the corrosion inhibitor, the hydrogen flux through the column wall was monitored with the Hydrosteel 6000. In total, 13 reading points were chosen on the soot-wash column K-201 (Figure 5), covering the damaged areas. As can be seen, flux at some sites initially exceeded 300 pL/cm²/s during an episode of high flux, prior to inhibitor treatment. From the temperature and thickness of the steel, it is possible, as in Figure 2, to deduce a hydrogen activity at such test sites in excess of 10^6 bar. Within a few days, the corrosion severity indicated by the flux monitor decreased typically by a factor of ten to 50. Since the hydrogen activity, expressed in bar molecular hydrogen, caused at a corroding surface is proportional to the square of a steady-state flux, this represents a 100–2500-fold decrease in the cracking propensity of the corrosion. Although there are certain test sites that are out of step with the general trend (eg, sites 1 and 2), data from all 13 sites suggest some episodes in corrosion increase; for example, between 40 and 60 days.

After positive evaluation of the test run, the customer decided to continue the treatment at both soot-wash columns and Kurita CI-6302 has been continuously applied to date. The performance of the treatment is controlled by measuring the hydrogen flux with the Hydrosteel 6000. During a turnaround, both soot-wash columns were inspected again, but this time no hydrogen damage was observed.

Conclusions

Hydrogen introduced into metals due to aqueous corrosion by hydrogen promoters can cause internal defects such as cracks, blisters, flakes, fish eyes, notches and porosity, which makes it a costly remedy. Under higher temperatures and high pressure, carbon steels may be weakened by decarburisation. In many cases, it is very difficult to evaluate the corrosion mechanisms, which often have overlapping characteristics. Hydrogen-induced fractures and cracks show similar characteristics to intergranular or transgranular cleavage fractures.

Corrosion monitoring is an essential tool to evaluate the current corrosion potential. Acidic corrosion usually requires several days for corrosive wall loss to be registered by the most sensitive thickness measurement methods, which do not directly measure the hydrogen activity generated by certain hydrogen promoters. Hydrogen damage can occur very fast, so a quick, reliable and accurate indicator of the propensity for hydrogen damage — the hydrogen flux — is essential. The hydrogen flux-monitoring technology evaluated in this work delivered these requirements and provides a user-friendly technical solution.

Higher steel qualities are more resistant to high-pressure hydrogen. Optimisation during metal production is also a good way of reducing the entry of hydrogen into the metal. There are cases where it is not possible to upgrade the metallurgy. Here, a suitable corrosion inhibitor such as Kurita CI-6302 can help to reduce the potential for corrosion. It forms a barrier between the metal and the atomic hydrogen. This results in a significant decrease in nascent hydrogen, which can permeate through the metal.

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