Measurement of hydrogen permeation through structural steel sections of varying thickness at 19°C

F. W. H. Dean*

Hydrogen permeation through four steel plates of varying thickness was achieved by simultaneously exposing one face of each plate to standard, sour corrosive conditions for periods of several days. A single representative structural steel had been used to mill the plates. The hydrogen flux at the opposing plate faces was measured using the hydrogen collection method. The work confirms that at low temperatures, hydrogen flux through a steel wall of greater than a few millimetres thickness is inversely proportional to thickness, all other factors being consistent. Furthermore, flux monitored from steel plate decayed approximately exponentially over the timescale of measurements, consistent with changing conditions at the steel entry faces. The work is of value in revealing how data generated by the probe fits with certain aspects of hydrogen diffusion and corrosion theory.

Introduction

Hydrogen cracking of steels is a major concern in steel processing and service, and occurs in several manifestations, such as cracking of rolled steel products, cold cracking of welds, and as a result of corrosion in sour (H_2S) environments. Information about the hydrogen level in steels is therefore very important, both during processing and in service.

The hydrogen content of steels can be measured by removal of steel for analysis, but this is time consuming and often impractical. Non-destructive test methods, engaging sensors or probes at a steel surface have been developed for measuring either electrochemical removal of hydrogen from the steel, or measuring freely evolved or effluxed hydrogen. Of the former type of measurement, the Devanathan cell is most representative.[1] In this work, an example of the latter was engaged, namely the hydrogen collection method.[2] The work was carried out at Swinden Laboratories, Corus UK to test the validity of some of the assumptions pertaining to the use of such flux measurement technology.

Measurement of hydrogen flux emanating from the surface of non-austenitic steels provides a means to monitor the propensity for hydrogen cracking in both laboratory and industrial environments. Hydrogen can enter the molten steel by reaction of water and other hydrogen bearing compounds in the molten steel, often introduced in feedstock. Atomic hydrogen can also enter steel at ambient temperatures, by electrochemical or chemisorption mechanisms, particularly in the presence of hydrogen promoters such as hydrogen sulphide, selenide, telluride, phosphide and arsenide, systematically evaluated with immersed steel samples by Newman and Shreir.[3] At both high and low temperatures atomic hydrogen is mobile, and migrates through the steel lattice under diffusion control. However, at ambient temperatures a proportion of the hydrogen is trapped in atomic form, predominantly at dislocations, grain boundaries, and surfaces of sulphides, carbides and voids. At critically high mobile hydrogen activities, hydrogen association to form molecular hydrogen occurs, leading to crack and blister initiation and propagation. Hydrogen in solution also leads to embrittlement, especially in hard microstructures. The propensity for hydrogen cracking is increased at decreasing temperatures, because:

(i) at decreasing temperatures, sites for hydrogen trapping are increasingly occupied, whereby hydrogen association is promoted;

(ii) the solubility of mobile hydrogen decreases with decreasing temperature, such that the mobile hydrogen activity at a given hydrogen concentration in steel increases markedly with decreasing temperature;

(iii) the diffusion of mobile hydrogen in steel decreases with decreasing temperature, retarding its rate of escape from the steel, and extending the time over which it can cause damage.

Thus in steel manufacture, hydrogen damage is chiefly associated with the period after processing when the steel is approaching ambient temperatures.

The hydrogen flux transient obtained from one face (the 'exit face') of a steel plate subject to a step change in

Ion Science Ltd, The Way, Fowlmere, Cambs, SG8 7UJ, UK

*Correponding author, email: Frank.Dean@ionscience.com
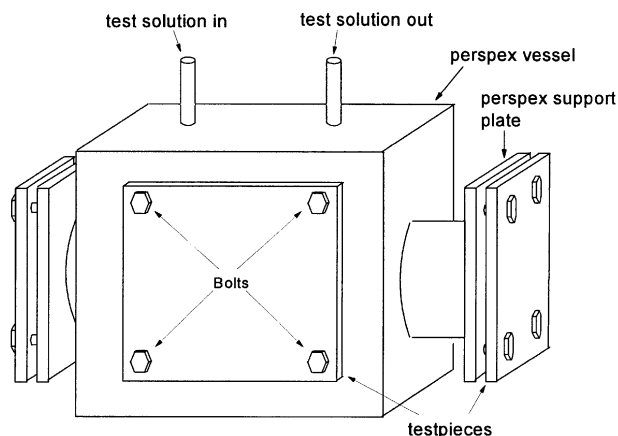
1 Schematic representation of experimental apparatus

Table 2 Test solution details

Test solution	%H$_2$S	%N$_2$
BP	50	50
	70	30
	85	15
NACE	40	60

hydrogen concentration at the opposite face ('the entry face') can readily be used to determine the coefficient for bulk diffusion D through the steel. Under steady state conditions, assuming D is concentration independent and the exit face subsurface concentration c_w of hydrogen is zero, the steady state flux J_{inf} through a plate of thickness w is determined by Fick's first law [4]

$$J_{inf} = D \frac{c_0}{w} \tag{1}$$

where c_0 is the invariant entry face subsurface hydrogen concentration. The assumption that c_w is zero is only strictly true for electrochemical removal.

In this work, the validity of hydrogen flux measurements obtained from the hydrogen collection method[2] are examined with respect to the theoretical expectations for w and c_0 in equation (1). One face of four steel plates of variable thickness w were simultaneously subjected to corrosive liquors containing sour gas at specific partial pressures determining c_0. The hydrogen flux J_{inf} emanating from the opposing, exit faces was monitored. Plates were removed and inspected after several days of exposure to each corrosive regime. By fitting modelled hydrogen flux transients to the observed transients, it was possible to estimate the concentration profile of hydrogen normal to each plate during the tests.

Experimental method

Material used in the present work was taken from the flange area of a universal column. The chemical analysis of this steel is shown in Table 1. Testpieces were fabricated to dimensions 150 mm × 150 mm × thickness w of 3, 6, 9, and 12 mm. One major face (area 150 mm × 150 mm) was retained in the as rolled (scaled) condition, whereas the opposite major face (also 150 mm × 150 mm) was ground to a 320 grit finish for all test pieces.

The test method employed in the present work involved exposing the ground testpiece face to solutions containing hydrogen sulphide using a test assembly fabricated from Perspex, as shown in Fig. 1. The test cell was designed to accommodate the four test pieces simultaneously. In each plate the area exposed to the corrosive liquor was approximately 100 cm^2.

Four testpieces with different thicknesses 3, 6, 9, and 12 mm were mounted in the assembly by means of bolts, and a seal against the Perspex chamber effected by means of a rubber 'O' ring. Basic test solutions were prepared from reagent grade chemicals and deionised water. The basic test solutions were BP and NACE solutions, details of which are shown below:

BP solution: synthetic seawater (ASTM D1141–90(96)), pH=5·0

NACE solution: 5% sodium chloride+0·5% acetic acid in distilled water, pH=3·0

With the testpieces in place, 5 L of test solution were purged of oxygen by bubbling continuously with nitrogen gas in a separate glass container. Hydrogen sulphide and nitrogen gas flow rates were then adjusted to provide specific gas mixtures, the details of which are presented in Table 2. The test solution was circulated through the test cell and glass reservoir over a period of up to 3 days by means of a peristaltic pump. Test solution temperature was maintained at 19 ± 1°C by enclosing the entire test assembly in a thermostatically controlled fume cupboard.

The hydrogen flux at each of the four test plate exit faces was intermittently measured during the course of the 3 day test using a device (Hydrosteel 6000, Ion Science Ltd, UK) based on the hydrogen collection method.[2] The device engaged a 'collector plate' comprising a flexible stainless steel plate with raised ridges, magnetically attached to the test steel surface. Air was caused to be drawn between the collector plate and test surface into a central capillary, and then across a hydrogen detector, by means of a pump downstream of the detector. The device delivered a flux J given by the expression

$$J = \frac{Fc_{air}}{A} \tag{2}$$

where F is the test gas flow, c_{air} is the concentration of hydrogen in the collected test gas flow relative to ambient air, and A is the effective steel surface area over which hydrogen is collected. The method is described in more detail elsewhere.[2]

Table 1 Chemical composition of the sample steel tested, wt-%

C	Si	Mn	P	S	Cr	Mo	Ni	Al	Cu	N	Nb	Sn	Ti	V
0·080	0·34	1·13	0·010	0·004	<0·02	<0·005	0·24	0·04	0·34	0·014	<0·005	<0·005	<0·005	0·10
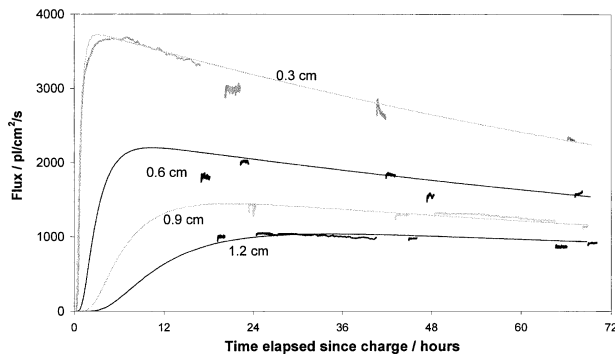
2 Typical set of transients obtained from one trial, showing transient test segments monitored and continuous modelled transient profiles

3 Initial entry face hydrogen concentrations versus plate thickness predicted from modelled diffusion profiles

Modelling flux profiles

To enable evaluation of the continuous flux profile for all four plates, based on intermittent measurements, modelling of the flux profiles was necessary. The model also allowed investigation of the rates of flux decay due to passive film growth at the hydrogen entry face. Model transients were obtained using a computerised iterative procedure based on Fick's second law[4]

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \qquad (3)$$
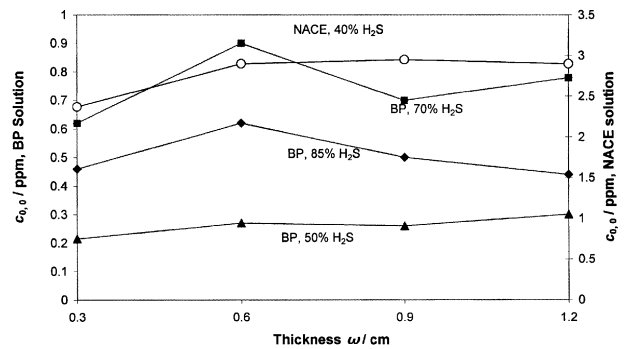
To optimise results the model progresses the hydrogen through the steel over sufficiently short time periods δt and sufficiently small thickness elements δx. Results computed by the program were confirmed for the efflux from a permeation plate under simple stepwise increase in concentration at the entry face by comparison with an exact solution derived by Crank.[4]

Transients obtained from all four test sections in a typical trial are shown in Fig. 2, together with modelled continuous transients for each test section. As can be seen, flux measurement was carried out on only one test section at a time so the transient for that test plate was measured intermittently. To obtain comparable sets of values, on occasion all four plates were tested within a short period of time.

In this work, designating t as the time since onset of hydrogen charging, and $c_{x,t}$ as the hydrogen concentration at distance x from the entry face at time t, the following boundary conditions were imposed:

  (i)   a concentration independent diffusion coefficient defined by Fick's law, of 5×10^{-6} cm^2 s^{-1};
  (ii) exclusively diffusion dependent hydrogen migration through the steel bulk;
  (iii) $c_{w,t} = 0$ for all t, that is, the exit surface concentration of atomic hydrogen is always zero;
  (iv) complete and rapid association of hydrogen at the exit face, and rapid desorption of molecular hydrogen thereafter;
  (v) $c_{0,t}$ for $t < 0$;
  (vi) $c_{0,t} = C_{0,0}e^{(-t/\tau)}$, where τ is a parameter describing growth of the sulphide film on the testpiece entry surface.

Condition (i) is an imposed diffusion coefficient, to enable comparison between the trial results. However, depending on steel composition, the diffusion coefficient of hydrogen in steel can vary.[5]

Condition (vi) was used to approximate the attenuation of hydrogen at the entry face caused by the formation of a sulphide film.

For a given test section, occasional data transient segments were lower than would be expected from the modelled results (see Fig. 2). It is likely that the reason for this was that the data was obtained when the collector head and the steel plate were not fully engaged, due to the very small clearance between the collector plate and the test section supporting nuts.

Results and discussion

Figure 3 shows the modelled hydrogen concentrations $c_{0,0}$ obtained for all four plate thicknesses, in the various corrosive environments investigated. Figure 4 shows the corresponding results $c_{0,44\text{ hr}}$ derived from equation (1), and thus assumes a uniform concentration gradient through the steel. The measurements were obtained 44 to 47 h after the onset of charging.

As might be expected, in comparing Figs 3 and 4, $c_{0,44\text{ hr}} < c_{0,0}$ for all the experimental regimes tested. The three BP regimes generated $c_{0,44\text{ hr}}$ values increasing with hydrogen sulphide content, for all thicknesses tested, apart from the 12 mm gauge plate results, whereas $c_{0,0}$ values for the BP 85% hydrogen sulphide regime were less than for the 70% regime at all gauges.

Hydrogen entry surface concentrations obtained from the NACE solution were considerably higher than from the BP solution, despite lower sour gas activity. This
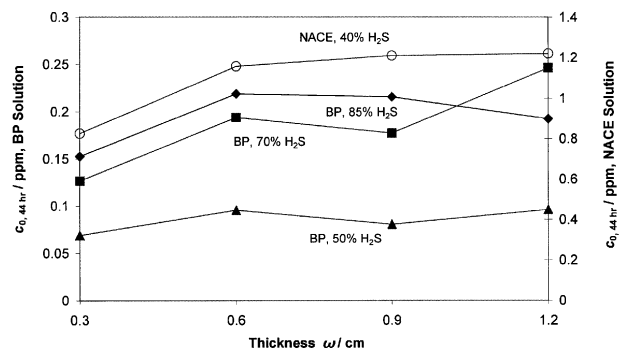
4 Hydrogen concentrations versus plate thickness predicted from modelled diffusion profiles 44 h after initial exposure
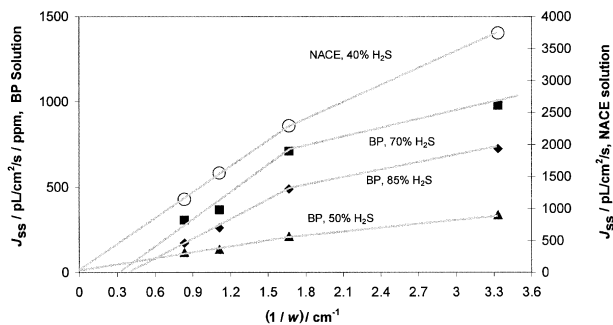
5 Relationship between steady state hydrogen flux and inverse thickness of test plates, for different sour environments

confirms the role of acidity in the promotion of hydrogen in steel,[6] the pH of pure NACE and BP solution being 3·0 and 5·0 respectively. The effect is particularly pronounced for the $c_{0,44\ hr}$ values (Fig. 4), where flux obtained from 40% hydrogen sulphide in NACE were in excess of five times greater than those obtained in 85% hydrogen sulphide in BP solution for all plates.

Modelled hydrogen entry concentrations as plotted in Fig. 3 and Fig. 4 are fairly independent of test plate thickness, consistent with both the model and expectations of plates exposed to identical charging conditions, simultaneously. However, significantly lower $c_{0,t}$ values were derived for the 0·3 cm plate in comparison with the thicker plates. This effect is also observed from plots of flux versus the reciprocal of test specimen thickness (Fig. 5 and Fig. 6).

Two interpretations to account for the observed behaviour are proposed. The 'exit' interpretation considers a limited density of surface states available for hydrogen exit. On decreasing w, a commensurate increase in flux at the exit face causes increasingly surface state saturation, and the subsurface hydrogen concentration increases from its near zero value at lower flux, such that flux J is no longer proportional to $1/w$.

The 'entry' interpretation considers an increasing steepness in the hydrogen concentration gradient through the steel as the thickness w is decreased. At some critical gradient given by

$$\frac{Dc_{0,t}}{w}$$

$c_{0,t}$ is no longer independent of w, as assumed above in the model, condition (vi) . Instead, in the prevailing experimental conditions, $w = 0\cdot3$ cm corresponds to the
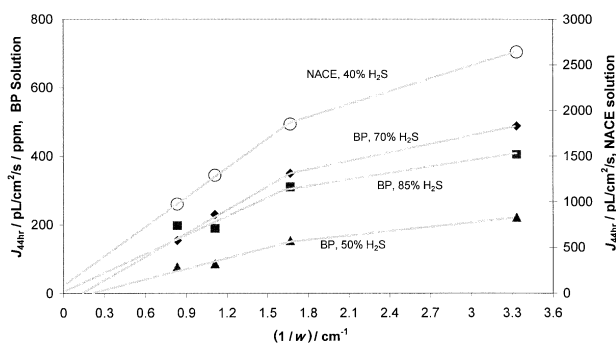
6 Relationship between hydrogen flux 44 h after saturation with specified concentrations of sour gas
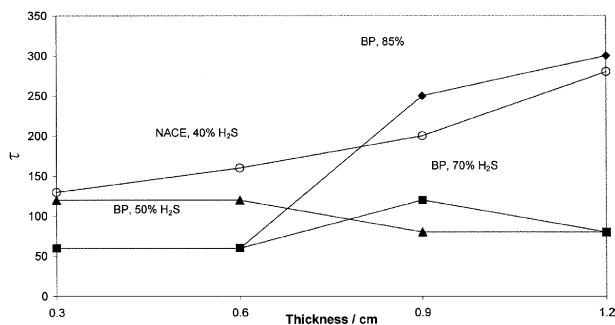
7 Model parameter τ versus w, where the model entry surface H concentration at time t after initial step to concentration $c_{0,0}$ is given by $c_{0,t} = c_{0,0}\ \exp(-t/\tau)$. Thus a low value of τ corresponds to a more rapid decay in response possibly due to more rapid sulphide film growth, or in the case of the NACE solution at pH 3, more rapid proton consumption.

onset of entry flux dependent kinetics. These kinetics dominate the behaviour of thin membranes, where flux becomes thickness independent. The interpretation is more consistent with the interpretation by Crolet *et al.*,[6] that an entry surface hydrogen concentration is not simply pinned at the surface by surface reactions, but is more dynamically dependent on hydrogen entry and exit flux at the corrosion interface as well as the flux into the steel interior.

Figure 7 shows modelled hydrogen entry concentration decay time constants for the various plates in the tested environments. There is some evidence for increased decay (lower τ values) at decreased w, particularly from the more robust flux profiles provided by the NACE solution. This supports the entry interpretation, since the rate of corrosion will be expected to increase with decreasing w only upon a decrease in $c_{0,t}$ provided by this interpretation.

The exit face could have a more significant effect as the inverse thickness $1/w$ approaches zero, as hydrogen flux decreases. At low flux, hydrogen association from the exit surface, being a second order reaction with respect to atomic hydrogen, is expected to become increasingly rate limiting, such that $c_{w,t}$ relative to $c_{0,t}$ increases, decreasing the concentration gradient, and causing flux to decrease relative to the inverse thickness dependency of equation (1). Also at low flux, hydrogen residence times at the exit face will be prolonged, and thus any reaction competitive with hydrogen association will increase in proportion (such reactions being first order with respect to hydrogen atoms). Further, it is well established that the effective diffusion coefficient for hydrogen in steels decreases with concentration, due to the decreased occupancy of traps a low concentration, decreasing flux permeation still further.

Figures 5 and 6 show this to the extent that some plots intersect the $1/w$ axis at a positive value. Again, the more corrosive NACE data is the least scattered.

Conclusions

1. Hydrogen flux through thicknesses of steel in the range 6 to 12 mm inclusive is inversely proportional to thickness, confirming that the data obtained using the flux probe conforms to accepted diffusion theory, namely Fick's first law of diffusion.

2. Data obtained from steel of thickness 3 mm does not obey Fick's first law of diffusion, and an explanation for this behaviour is presented in terms of hydrogen entry face considerations.

Acknowledgements

References

1. M. A. V. Devanathan and Z.Stachurski: *Proc. Royal Soc A*, 1962, **270A**, 90.
2. F. W. H. Dean and D. J. Fray: *Mater. Sci. Technol.*, 2000, **16**, 41.
3. J. F. Newman and L. L. Shreir: *Corros. Sci.*, 1969, **9**, 631–641.
4. J. Crank: 'The mathematics of diffusion', 2nd edn, Oxford, UK, Oxford Science Publications.
5. H. J. Grabke and E. Riecke: *Mater. Tehnol.*, 2000, **34**, 331–342.
6. J. L. Crolet and M. R. Bonis: 'Corrosion 2001', NACE Conference, Houston, TX, 2001, Paper 01072.