

HYDROGEN FLUX AND CORROSION RATE MEASUREMENTS ON HYDROGEN INDUCED CRACKING SUSCEPTIBLE AND RESISTANT A516 STEELS IN VARIOUS SOUR ENVIRONMENTS

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ABSTRACT

Two A516 16 mm plate steels were simultaneously exposed to various sour saturated solutions at 20°C over two week trials. One plate was known to be highly resistant to HIC cracking, the other to be highly susceptible to HIC cracking. Flux and corrosion rates of the two plates decreased after a few days in non-buffered acid solutions, whereas in buffered acid conditions they maintained a steady state. Crack surface ratios of HIC susceptible plates post-trial were approximately proportional to the total wall flux passed. In ammonium bisulfide solutions, flux was only induced by addition of cyanide. In all trials, flux from the two plates co-trended extremely closely. Computed hydrogen diffusivities, entry concentrations, and permeabilities of the HIC resistant and susceptible plates were similar. Diffusion coefficients varied between 8 and 12 x 10^{-6} cm².s⁻¹, consistent with other data for A516 steels. There was good correlation between corrosion rate and steady state flux for the first day of measurement, except from pH 2.7 solutions, where an additional, non-hydrogen occluding corrosion of 0.5 mm/yr corrosion rate was attributed to similar corrosion measured prior to sour saturation. Apart from this, no pH effect on the correlation was evident between pH 2.7 and pH 9.

Key words: hydrogen permeation, hydrogen flux, hydrogen induced cracking, crack ratio, sour corrosion.

OBJECTIVES

The objectives of the work reported here, were to correlate corrosion rate and hydrogen flux through simultaneously tested hydrogen induced cracking (HIC) susceptible and resistant A516 grade steels in sour solutions at ambient temperatures, and to investigate the influence, if any, of plate HIC susceptibility and damage, on through wall hydrogen flux.

INTRODUCTION

Hydrogen flux measurements on sour corroding steels are performed in the laboratory to study:

• Steel susceptibility to HIC

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- Conditions which increase or decrease sour corrosion and HICVED
- The effectiveness of inhibitors or barriers in preventing sour corrosion
- The correlation of flux measurements with corrosion rates
- Steel HIC susceptibility is the objective of most studies presented in the literature and accordingly, emphasis is placed upon hydrogen in steel bulk, as characterized by a steel's hydrogen diffusion D (cm²/s) and solubility S (ppm wt/wt, but see Table 1a for other units)¹ obtained from hydrogen permeation measurements.

The rate of diffusion of hydrogen in a metal is proportional to the concentration gradient of *mobile* hydrogen in the metal, according to Fick's Law. If the diffusion is in one dimension (*eg* through plate):

$$J = D dc/dx$$
(1)

where flux J is measured in pL/cm²/s (see Table 1b). D can be obtained from (1) by modeling a measured flux profile caused by a step increase in sour corrosion, as in this work, or step increase in applied cathodic current. It is then possible to obtain the entry face mobile hydrogen concentration c_o ,

$$\mathbf{c}_0 = J_{ss} . (\mathbf{w}/\mathbf{D}) \tag{2}$$

To apply equation (2), the steady state flux should be converted to $Ncm^3.cm^2.s^{-1}$ (Table 1b) and c_0 from $Ncm^3.cm^3$ to ppm (Table 1a). Equation (2) can be derived from (1) at steady state, that is, when a uniform mobile hydrogen concentration gradient is established through a steel, *assuming* the exit face sub-surface concentration (c_w) is zero, *and* the diffusion coefficient is independent of concentration. Some literature examples are presented¹⁻¹⁴ in Table 2. For the hydrogen collection method of flux measurement technology used in this work, the validity of these assumptions has been broadly demonstrated^{15,16}. However, close examination of flux profiles reveals that diffusion is in fact concentration dependent^{17,18}; an increasing concentration of mobile hydrogen in steel increases hydrogen mobility as trap occupancy increases.

D values are primarily used to determine entry face mobile hydrogen concentrations c_0 according to equation (2). In principle, concentration thresholds can then be cited for particular steels at which cracking can occur, or as indicators of corrosion severity. This is superficially attractive in that steel manufacturers cite concentrations of *trapped* hydrogen, as a key specification parameter. Trapped concentrations of hydrogen exceeding 1 ppm present a threat of hydrogen damage in downstream applications, particularly during welding of larger steel components. There appears not to be a simple correlation between D or c_0 and crack susceptibility however. This is largely due to the sensitivity to microscructure and inclusions. Also at the temperatures of sour aqueous corrosion, concentrations of mobile hydrogen generated within a steel – a few ppm – are comparable to typical concentrations of hydrogen in trap sites, which may pre-figure in the onset of HIC, or be entirely benign. This somewhat limits the value of laboratory flux measurements to characterize the susceptibility of a steel to crack.

Most hydrogen flux measurements have been carried out with the Devanathan-Stachurski cell in which one side of a steel membrane – the entry face - is exposed to hydrogen charging conditions and the other exposed to a solution which enables the any hydrogen flux exiting the membrane to be measured as an anodic current. The measuring side of the circuit typically delivers a flux to a resolution of typically 0.1 μ A.cm⁻² (12 pL.cm⁻².s⁻¹), although sensitivities as low as 0.3 and 3 pL.cm⁻².s⁻¹ are reported ^{7,18}.

The objective of this work is to consider the sour corrosion induced behavior of hydrogen flux through steels of very different HIC susceptibility, and explore how D and s, flux J itself, or some other parameter might be used to indicate the HIC severity of sour corrosion *independent* of the steel under test. Moreover, it was hoped the work might clarify whether – or when - flux measurements may provide a useful measure of sour corrosivity. In view

⁽¹⁾ Note pL are quoted at 20 °C and 1 atmosphere, 1.013 bar, whereas Ncm³ at 0 °C and 1 bar, hence the non-unitary conversion. 1 mol ideal gas occupies 22.414 L at 0 °C and 1.013 bar.



of the latter, the hydrogen collection method was used in this work, being recognized as a technique that could be used in the field. The sensitivity of the technique is similar to electrochemically measured flux.¹³ However, the use of a different measuring technique in the laboratory will be discussed.

EXPERIMENTAL PROCEDURE

Two steels were mainly employed in this work, as specified in Table 3. For each trial, plates were machined equally on both sides to 16 mm thickness and 200 mm square. They were then shot blast to Sa 2.5, and assembled in the corrosion tank illustrated in Figure 1. A commercial hydrogen flux analyser⁽²⁾ was used to continuously monitor hydrogen flux from the external surface of each plate, using magnetically attached identical hydrogen collection probes (150 mm, 6 in diameter). Zero flux was registered from both plates, in every trial, prior to exposure to corrosive solutions. The monitors were powered by means of a mains adaptor, and set to continuously monitor (data intervals being 10 every minutes after 2 hr continuous monitoring)

The tank was filled with 26 liters of corrosive solution detailed in Table 4. Solutions were prepared according to the identified standards in separate de-aeration chambers, purged with white spot nitrogen overnight prior to admission to the corrosion tank. Within an hour, at time t = 0, 99.5% hydrogen sulfide, balance nitrogen was introduced at a rate of 3000 ml/minute for 1 hour and 250 ml/min thereafter.

On a daily basis, measurements of corrosion rate and corrosion potential using a linear polarization resistance (LPR) bullet probe. A+- 10 mV sweep was employed, and the LPR, R_p , determined from the Stern-Geary equation,

$$\mathbf{R}_{\mathrm{p}} = \mathrm{d}\mathbf{E}/\mathrm{d}\mathbf{i} = \beta_{\mathrm{A}}\beta_{\mathrm{C}} / \{ 2.3(\beta_{\mathrm{A}} + \beta_{\mathrm{C}}) . i_{\mathrm{CORR}} \}$$
(3)

where β_A and β_C are the Tafel slopes for anodic and cathodic reactions (4) and (5) respectively:

$$Fe \rightarrow Fe^{2+} + 2e$$
 (4)

$$\mathrm{H}^{+} + \mathrm{e} \to \frac{1}{2} \mathrm{H}_{2} \tag{5}$$

And typically had values of 13.5 and 15 mV respectively. Steel wall loss in mm/yr was then linearly derived from the Faradaic removal of iron according to reaction (4). LPR probe measurements were IR compensated.

Evidence of hydrogen damage was registered by routine manual UT inspection. At the end of each experiment certain steel specimens were sectioned to determine the crack surface ratio, CSR according to the standard test procedure NACE TM0284¹⁹. In brief, the crack length ratio, CLR, expressed as a percentage, is obtained from the length of cracks in mm obtained per 20 mm width, x 100. The crack thickness ratio, CTR, is obtained from the crack thickness in mm divided by the specimen thickness, x 100. The CSR, is given by the total crack surface area divided by total coupon cross sectional area.

RESULTS AND DISCUSSION

Overview

A summary of experimental results are presented in Table 5 (see also Table 4) and illustrated in Figures 2-11. Columns of data are obtained as follows. 'Trials' are designated according to independent conditions. The qualifier 'a', b' refers to repeated trials. Two pre-trials, 0b and 0c are deemed worthy of consideration below. Solutions prepared, according to standard procedure are cited, together with solution pH at the start of test. 'Purge' refers to the time for which the plate steels were exposed to solutions purged with nitrogen prior to sour gas exposure. Subsequent data is presented for the two plates stationed at corrosion chamber positions A or B. For each plate, 'cracks' are affirmed where detected and verified by ultrasonic testing. The maximum measured

⁽²⁾ Hydrosteel 6000 with LT-R collector, Ion Science Ltd, UK

IN A PPROVED

flux and corrosion rates are identified, together with corrosion rates obtained prior to the onset of sour corrosion. Italicized data were obtained from a simple flux modeling program incorporating Fick's first Law, equation (1), with boundary conditions of zero mobile hydrogen concentration for all steel depths prior to some time t = t(delay) after hydrogen sulfide exposure at t = 0, and constant sub-surface entry hydrogen concentration c_0 , for all times t > t(delay). t(delay), D, and c_0 were optimized to fit measured flux data and respectively entered in Table 5. An example of modeled data is shown in Figure 2.

Measurement Integrity

In early tests (to Trial 1a) electrical apparatus was found to degrade considerably in the low ambient concentration of sour gas present in the laboratory environment, even though sour gas was considered not to exceed a few ppm. Instrument monitoring was prone to terminate on brief interruptions of the power supply. The other key issue regarding flux monitor performance related to temperature compensation. The internally monitored temperature displayed in Figures 4 to 7 shows near coincident diurnal changes in temperature and flux, of approximately \pm 3 °C and \pm 5% respectively. The flux monitor measurement was internally temperature compensated. There are several other temperature effects which may have contributed. Firstly, although only a fraction of a degree of ambient change may have been experienced by the corrosive solution, it might be expected to increase hydrogen entry due to increased corrosion rate and increased hydrogen entry kinetics. Secondly, an average steel wall temperature increase of just two degrees will increase its hydrogen permeability by some 11%. This underlies the importance of steel temperature measurement in the correlation of hydrogen flux measurements.

The linear polarization resistance (LPR) measurements were considered generally dependable in sour environments studied, using independent electrodes, not an integrated probe. In Trial 6a, a non-zero corrosion rate registered from the metalized plate 5, averaging 0.086 mm/yr, probably represents a typical base line error in LPR measurement, as such a corrosion rate would be expected to deliver a flux of some 20 pL.cm⁻².s⁻¹ whereas <3 pL.cm⁻².s⁻¹ was measured. The reliability of corrosion rate measurements in cyanidic environments, Trials 4a and 5a, is discussed further below.

During the project an acoustic listening system for detecting hydrogen crack incidents was tested. The system was compromised by the difficulty in retrieving crack signals from an overwhelming volume of spurious background, particularly attending bubble bursting in the corrosive solution.

A very sensitive, continuous thickness gauge UT monitor was reviewed at one stage as a means of capturing crack onsets. The gauge was prone to dis-bonding due to hydrogen flux.

Diffusion Coefficients and Entry Face Hydrogen Concentrations

Flux data from all trials is modeled as shown in Figures 2 to 11. Deduced values of *Jss*, t(delay), D and c₀ are shown in Table 5. It is thought that t(delay) corresponds mostly to the time required for infilling of traps within the 16 mm plate. There may be some initial time for dissolution of surface oxides but this is considered minor because profiles on thin plate in similar conditions are found to be small.

Comparison of Figures 3 to 11, indicates a good fit of flux predicted from pure Fick's diffusion through the 16 mm plates and measured flux, especially when it is considered that steel plate was not pre-charged with hydrogen. Modeled data in Table 6 show over almost seven orders of magnitude of pH change, values of D lie within 20% of 10 x 10^{-6} cm²/s, in reasonable agreement with figures for some low alloy steels obtained from the literature¹⁰, Table 2, though they are significantly higher than *eg* Hay's values⁵. Table 6 flux onset delay times t_{delay} for plate 5 show some increase with pH which could relate to the stability of oxides on the surface at higher pH, but the effect was not discernable from Plate 3.

Generally, compared with the values of Jss.w, D and c_0 obtained in this work, Table 6, mild steel data drawn from the literature in Table 2 indicates at 20-25 °C,

- lower *J.w* (flux thickness) values, especially for thinner steels (w< 3 mm)

- diffusion coefficients D which are approximately three to five times lower, and
- c_0 values which are similar.

Unlike anodic stripping of hydrogen flux in a Devanathan-Stachurski cell, the hydrogen collection method of flux measurement requires spontaneous desorption of hydrogen from the exit surface, almost certainly of molecular hydrogen, at the exit face. There might therefore be expected to be a significant hydrogen concentration at exit face, leading to a decrease in the concentration gradient of hydrogen through steel, and thus lower flux. However, electrochemical measurements may be prone to lower flux on account of the use of a Pd or Ni film at the exit face, which are commonly used to prevent anodic oxidation of iron. This would decrease the diffusivity of the membrane, decreasing the apparent diffusivity of the steel iteself. Such a decrease in D values is commonly seen with the Devanathan-Stachurski cell.

A further consideration is thickness of membrane used. Cell design considerations have led to most experimenters to deploy membranes of a small hydrogen entry surface area. In order to avoid edge effects (and to maximize flux), thin steel membranes are deployed ($\mathbf{w} \sim 1$ mm). Now, under identical hydrogen charging conditions, the steady state flux J_{ss} generated through-wall increases inversely with decreasing thickness \mathbf{w} according to equation (2), *ie Jss*. \mathbf{w} should be constant, so long as the mobile hydrogen entry concentration c_0 is invariant. However, at some critically decreased thickness threshold \mathbf{w}_{crit} , flux increases to an extent that the concentration of hydrogen at the entry face, c_0 is no longer defined by surface reaction kinetics, and begins to decrease. \mathbf{w}_{crit} may thus be rate-determined by a number of dynamic factors, such as the rate of hydrogen generation at the entry surface, its entry sub-surface, hydrogen solubility s, hydrogen recombination at the entry surface, and, indeed, hydrogen exit surface dynamics.

Bockris²⁰ presents data for cathodically biased steel in 0.1 M sulfuric acid for which $\mathbf{w}_{crit} = 0.5$ mm. Asahi *et al.* data¹² indicate $\mathbf{w}_{crit} = 1$ to 1.5 mm, under conditions of much higher entry flux. More recently, Kittel *et al.*¹³ indicate a value of $\mathbf{w}_{crit} = 2$ mm. In consequence of this effect, *Jss.* values using membranes of < 2 mm tend to be low. Using the hydrogen collection method, Dean¹⁴ obtained $w_{crit} \sim 4$ mm. This higher value may arise from hydrogen collection requiring molecular hydrogen desorption at the exit face, causing a non-zero exit face concentration and more sensitivity to changes to c_0 . However, with 0.5 mm membranes Bonis and Crolet²¹ and Kittel *et al.*¹³ report close agreement in sour corrosion induced flux obtained electrochemically and with the collection method. Furthermore Tems *et al.*⁹ report close flux-thickness correspondence with Devanathan experiments using 0.75 to 0.82 mm films as compared with the collected flux from 13 mm thick HIC resistant steel, simultaneously exposed to the same sour environment. So the need for surface hydrogen desorption on sour corrosion induced flux measurement using the collection method is not critical.

Finally, values of c_0 computed from (2) may be subject to two opposing artifacts, using too thick a coating, and too thin a membrane. We note Hay⁵ delivers values of c_0 which are highest for the thickest steel tested, namely Line Pipe 1, at **w** = 4.84 mm. For this steel, solution A (NACE TM0284 pH 5) delivers c_0 of 1.1 ppm, comparing favorably with the Trial 3b (ditto, pH 4.5), of 1.5 ppm. As expected from the discourse above, D values for all line pipes reported by Hay are lower than those obtained by ourselves. Laycock *et al* D values¹⁰ are notably higher than others using Sevanathan cells in Table 2. This may be due to the use of a nickel flash prior to palladium plating by the authors.

Hydrogen Damage – Similarities in Flux Profiles Obtained from a HIC Resistant and Susceptible steel

A question arising in this work was whether hydrogen damage altered the profile of hydrogen flux. Many of the trials therefore engaged one steel plate, 4 or 5, known to suffer HIC and a second plate, 3, known to be resistant to HIC. Consistently, within a few days of sour corrosion Plates 4 and 5 developed HIC cracking blisters at a depth of 4 to 10 mm from the corroding face as expected, whereas careful UT examination of Plates A revealed no evidence of damage whatsoever, even after the completion of each trial. Examples of hydrogen cracking are shown in Figures 13a and 13b. The flux data shows very close trending through the two steels tested. There was no evidence of abrupt decreases in flux corresponding to crack onset from HIC susceptible plate although the crack ratios discussed below were probably too low for a significant decrease in activity – and hence exit face flux - in these plates to occur. One might at least expect progressive damage of Plate 4 or 5 to cause flux to decrease

relative to Plate 3. The profiles of the continuously hydrogen occluding buffered solutions of Trials 2a and 3b, Figure 6 and 7, shows some evidence of this, but the equally severe trial 0c with Plate 4 steel, Figure 4, showed no such trend.

Another widely held intuitive expectation is that a crack resistant plate will prevent flux throughput by delaying hydrogen in traps. It can be seen from Table 5 that under the same corrosive conditions, Plate 5, which consistently cracked, delivered flux transients D and c_o values which were *higher* than those derived from the flux transients of a crack resistant plate. No clear correlation between HIC susceptibility was found in a similar investigation by Cayard⁶, either. It is clear that values of D, still less c₀, are not of themselves good indicators of crack susceptibility of steel plate, because they indicate a degree of both benign and deleterious hydrogen trapping.

As Grabke and Riecke found on reviewing a number of steels¹⁷, permeability is much less susceptible to steel differences than diffusivity D and solubility S. In fact, an increase in trap density increases hydrogen solubility and decreases diffusivity D, broadly in inverse proportion, so permeability P=D.S is not so affected by steel variance. Indeed the flux profiles from HIC susceptible plate 5 would indicate that it was slightly more hydrogen permeable than Plate 3.

Table 6 summarizes crack analysis on three equidistant sections of the crack susceptible Plate 5 HIC coupons . Also included is the total flux collected over the course of the two week trials where such data was obtainable. Figure 12 shows that the average CSR correlates well with the total hydrogen collected, despite scatter in the independent section crack data in the table. Flux maxima for all trials were very similar. However flux and corrosion rates from unbuffered solutions tended to decrease after a few days of proton consumption. Probably, while crack initiation onay particular steel might require an initial critical H activity threshold within a steel, thereafter crack propagation is proportional to H activity summed over time exceeding a much lower threshold. Thus for Plate 3 we see no cracks since the activity threshold for crack *initiation* in this HIC resistant steel was never exceeded, whereas 5 data in Figure 12 identifies a total flux prevailing where activity threshold for crack *propagation* was always exceeded.

Figure 13 illustrates the Trial 6a, Plate 5 coupon sections, shown together with a 65 mm wide section of the Plate 5 used (corroding face uppermost), with two cracks evident., Figure 13b. The plate CLR=11.4%, CTR= 2.81%, CSR=0.16%, which was much lower than the coupon. This is expected in view of one sided charging of the plates, as compared with full immersion of the coupons. Thus for example Newman and Shreir obtain a bulk hydrogen concentration of 2 ppm from full immersion of plate in 0.1 N NaOH + 0.1 g/L Na₂S, subject 0.5 mA.cm⁻² cathodic bias³, whereas, Luu *et al.* ² obtain only 0.85 ppm from 0.1 N NaOH + 1 g/L Na₂S at 10 mA.cm⁻² for one sided charging.

In Figure 14, microstructural sections of Plates 3 and Plate 5 are compared, together with a Plate 5 crack in detail. In both cases large ferritic grains and pearlitic banding is evident.

In conclusion, flux prevailing from a HIC susceptible A516 grade steel Plate 5 were neither in magnitude nor profile significantly different from flux from an A516 grade steel HIC resistant Plate 3, during the onset of cracking in the former plate by sour corrosion. Continuous flux monitoring cannot therefore be used as a means of diagnosing early HIC onset, any more than other methods reviewed. On the other hand, hydrogen activity calculated from flux magnitude, temperature and thickness is liable to provide a good indicator of the propensity of a particular corrosion scenario to damage HIC susceptible steels in so far as permeabilities of these and resistant steels do not vary widely.

Correlation of Corrosion Rate with Hydrogen Flux Model Data

Nanis and Namboodhiri¹⁸ identify an increasing proportion of hydrogen permeates steel relative to the cathodic current producing hydrogen at the surface. This is expected in that recombination, by which hydrogen bubbles off, is approximately second order; it is likely to increase as the square of the surface hydrogen concentration. Likewise, we anticipate and find that flux increases less than proportionately with increasing sour corrosion rate.

UNAPPROVED is obtained from model steady state flux obtained from the model

A reasonable correlation is obtained from model steady state flux obtained from the model data in Table 5 and equation (2), and LPR determined corrosion rates approximately 48 hr after sour exposure. This is shown in Figure 15. The correlation line is given by the semi-empirical equation

$$J = 10900c \cdot \alpha \cdot (1 - Ac^{1.2})$$
(6)

where *c* is the corrosion rate in mm/yr. The factor 10900 relates to conversion of *c* to mol Fe.cm⁻².s⁻¹ and of *J* to mol H₂.cm⁻².s⁻¹, from which, and assuming at the corroding face iron is oxidised to Fe(II) species in equimolar ratio with the reduction of 2 protons (4, 5), the hydrogen occluding efficiency, *ie* fraction of hydrogen entering steel, of the corrosive solution tested on 16 mm steel, $\alpha = 0.076$. The term (1-Ac^{1.2}), with A = 0.77, is included to generate some curvature in the profile, which will invariably occur at higher cathodic corrosion current densities as the recombination of hydrogen is increased by reactions such as:

$$H_{Fe} + H_{Fe} \rightarrow H_2 \text{ (desorbs).}$$
(7)

Figure 15 shows corrosion rates to exceed flux indicated by the correlation line for data obtained at pH 2.7, by about 0.5 mm/yr. This is similar to the corrosion rates obtained from the LPR probes obtained from solutions stabilizing at pH 2.7 *prior* to H_2S saturation, Table 5. Further confidence in the correlation line is realized in the intermediate offset of unbuffered pH trial 2a data, for which the pre-sour corrosion rate was again some 0.5 mm per year, which equilibrated at pH 3.6 within hours of sour exposure, Figure 6.

Thus we conclude from the modeled data that the correlation of flux with *sour* corrosion rate appeared to be very weakly dependent on pH over some seven orders of magnitude in pH.

Correlation of Flux with Coincident Corrosion Rate

The actual flux measured coincident with corrosion rate at times t > 48 hr is presented in Figure 16, together with the same correlation line presented above. Again, pH 2.7 trial data shows an approximate 0.5 mm/yr shift from the correlation line, as discussed above. This does not severely compromise field use of low temperature flux measurements, in so far as pH 2.7 sour solutions are not commonly encountered.

Further, although pH 8-9 data is low as compared to the model, this is readily understandable in terms of the transience of the corrosion episode, as illustrated in Figure 9 and Figure 10, Trial 5a, whereby a high entry transient flux was 'smoothed' by through 16 mm wall permeation through the substantial thickness of plate deployed. The same intense hydrogen entry flux was likely in trial 4a: it is indicated by the close correspondence of Trial 5a data superposed on Trial 4a spot measured data, Figure 8. Indeed, the strong resemblance of these plots suggests the agency of cyanide as removing iron sulfide film at pH > 5, rather than promoting hydrogen flux itself. Thus low flux values at high pH data relative to the correlation curve in Figure 16 are probably due to flux not being at steady state. Similar behavior is observed by Wilhelm and Abayathnaya¹, who obtained slightly lower maximum flux-thickness values as trials 4a and 5a under similar cyanidic solutions. Much higher and sustained flux may be (and indeed have been) expected in a field environments where subject steel is continuously exposed to cyanide. In such environments the correlation would be useful.

The remaining prospectively anomalous data encircled in the corrosion rate flux plot Figure 16, is from Trial 2a, Plate 5, for which an abrupt decrease in LPR corrosion rate between t = 113 and 121 hr, is not reflected in either the flux transient, Figure 9, but is reflected in the corrosion potential, Figure 17. Indeed, corrosion potentials and rates (recorded together) in Figure 17 show good correspondence for all coincidently measured Plate 3 and Plate 5 data (some of the times *t* of which are indicated on the Figure), except for trial 2a, Plate 5, t > 120 hr. For this 'problem' corrosion rate data the Tafel slopes used in Sterne Geary relationship, equation (9) were probably not reliable, and so neither were the calculated corrosion rates. From a thermodynamic standpoint, FeS is not stable in the pH range of Trial 2a, (2.7 to 3.8), but the progressive formation of sulfur and polysulfides most certainly is

predicted as the rest potential increased from -400 to -200 mV. It is also notable that at t < 0, Trials 1a and 2a solutions were both pH 2.7, but corrosion potentials for Trial 2a were much lower.

The flux-thickness magnitudes obtained in this work, are generally in good agreement with literature values from sour systems, Table 2, given that decreased flux thickness values (J.w) are expected and obtained from the thinner membranes. The congruence of our results with Shimitzu *et al.*⁸ on 8.77 mm thick line pipe in very sour solutions is reassuring.

CONCLUSIONS

- 16 mm plates of two steels were simultaneously exposed to various sour saturated solutions, at 20 °C, for two weeks. One did not show any evidence of hydrogen induced cracking (HIC), the other consistently cracked.
- 2. Flux and corrosion rates of the two plates decreased after a few days in non-buffered acid solutions, whereas in buffered acid conditions they reached and maintained a steady state for two weeks. After these trials, the crack surface ratio (CSR) of four sectioned, HIC susceptible plates were approximately proportional to total through wall flux passed, suggesting crack initiation in the first few days of exposure, and progressive cracking proportional to flux passed, thereafter.
- 3. In ammonium bisulfide solutions, flux was only induced by addition of cyanide; the flux then subsided, probably due to reaction with sulfide.
- 4. In all trials, flux from the two plates co-trended extremely closely. A significant diurnal temperature effect was observed consistent with steel temperature variation of a few degrees, underlying the temperature sensitivity of hydrogen permeation.
- 5. Early modeled flux data from the trials indicated the hydrogen diffusivities, entry concentrations, and permeabilities of the HIC resistant and susceptible plates were similar. Diffusion coefficients varied between 8 and $12 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, consistent with other data for A516 steels.
- 6. There was good correlation between corrosion rate and steady state flux obtained from modeled data pertaining to the first 24 hr of measurement, except from pH 2.7 solutions, where an 'additional', non-hydrogen occluding corrosion of 0.5 mm/yr corrosion rate was attributed to similar corrosion measured prior to sour saturation. Apart from this no discernable pH effect on the correlation was evident between pH 2.7 and 9.
- 7. The same correlation curve was approximately observed between coincidently measured flux and corrosion rates, when allowance was made for pre-existing sour corrosion at low pH, and the brevity of a flux episode at high pH.
- 8. The flux corrosion rate correlation was also consistent with a previous study using 3 mm steel, *ie* sour corrosion induced flux depended inversely on thickness.

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TABLES

TABLE 1A:	CONVERSIO	ON OF UNITS	OF H IN STE	EL CONCENTRATION
$1 \text{ pL.cm}^{-2}.\text{s}^{-1}$	$1 \mu\text{A.cm}^{-2}$	10^{-12} molH.	10^{-9} Ncm ³ .	
=	=	$cm^{-2}.s^{-1} =$	$cm^{-2}.s^{-1} =$	
1	124.6	12.02	1.06	pL.cm ⁻² .s ⁻¹
0.00802	1	0.0965	0.00850	μ A.cm ⁻²
0.0831	10.36	1	0.0881	$x10^{-12}$ mol H.cm ⁻² .s ⁻¹
0.944	117.7	11.35	1	$x 10^{-9} \text{ Ncm}^3 \text{.cm}^{-2} \text{.s}^{-1}$

TABLE 1B: CONVERSION OF UNITS OF HYDROGEN FLUX

	mi bilo obi i		e e i i i i i i i i i i i i i i i i i i		
	1 μmol H.cm ⁻³	$10^{18} \text{ atoms .cm}^{-3}$	$1 \text{ Ncm}^3 \text{ cm}^{-3}$	1 ml / 100 g	1 ppm by wt
	=	=	=	=	=
ppm by wt	0.127	0.211	11.21	0.816	1
ml/100 g ¹	0.156	0.259	13.7	1	1.225
Ncm ³ .cm ⁻³	0.0114	0.0189	1	0.073	0.089
$x \ 10^{18} a toms \ .cm^{-3}$	0.602	1	53.0	3.86	4.73
µmol H.cm ⁻³	1	1.66	88.1	6.41	7.86

TABLE 2. SOUR CORROSION INDUCED FLUX DATA PRESENTED IN THE LITERATURE. co VALUES ARE GENERALLY DEDUCED FROM *Jss*, D AND w USING EQUATION (2). WHERE NO SUCH VALUES ARE PRESENTED, ONE OF THESE QUANTITIES IS NOT IDENTIFIED

ref	steel	Composition	w/ mm	Are a /	T / ℃	entry electrolyte	I _c / mA. Cm ⁻²	Coat µm	Exit electrolyte	Jss / pL.cm ⁻² s ⁻¹	J.w/ $L.cm^{-1}s^{-1}$	D / 10 ⁶ cm ² . s ⁻¹	c ₀ / ppm
1	A516 grade	'low sulfur'	0.75	cm ²		1M NH₄OH sat.H₂S + 5000 ppm	0.083	[600	[Not cited]	2867	215	-	
2	70	C 05 Si 067 Mp 22	0.8	10	25	$CN^{-} > pH 7.9$	10	grit]		1047	81	1.04	840
2	mild	S.01	0.8	10	23	$0.11N \text{ NaOH, } 1g/L \text{ Na}_2S$	10	.2 Fu		1047	04	1.04	.049
3	h. strength REX539		2.54	5	25	6mg/l NaAsO ₂ in .1N NaOH 6mg/l NaAsO ₂ in .1N H ₂ SO ₄	0.5	no	300 °C vac. extract	-			7 11
						>.1 g/l Na ₂ S in 0.1N NaOH >.1 g/l Na ₂ S in 0.1 N H ₂ SO ₄	0.5			-			2 10
4	UNS S41000 ss type 410	C.14, Si.32, P .02,Cr 13.5, Mn.46, S.007, Ni.71, Mo.05, Cu.15	0.7	4.8	23	5%NaCl + CH ₃ COOH + sat. H ₂ S = 4000 ppm. pH 2.6	corr.	no	0.1N NaOH	3366	232		.032
	Line pipe 1	C.14,Mn1.02, Si.01, S.14, P.006, Cu.03, Ni.02, Cr.03	4.32	3.8	25	A-E, All sat. H ₂ S @1 bar: A, pH 5: ref. 19 B, pH 4.1: 5%NaCl,1%CH ₃ COOH C: pH 3.1: SCL IIIC D: pH 3.5, acetic buf. 5% NaCl E: pH 2.5 NACE TM0177 ²²	corr.	no	0.2N NaOH	611 845 976 1434 1446	260 360 416 611 616	2.49	1.12 1.55 1.79 2.64 2.65
5	Line pipe 2	C.18, Mn.78, Si.01, S.19, P.006, Cu.02, Ni.02, Cr.02	1.75	3.8	25	A – see above B C E	corr.	no	0.2N NaOH	622 649 974 1346	107 112 168 232	5.0	.230 .240 .360 .500
5	Line pipe 3	C.148, Mn.76, Si .01, S.14, P.006, Cu .02, Ni.02, Cr. 02	2.01	3.8	25	-	corr.	no	0.2N NaOH	-		7.5	-
	Line pipe 4	C.18, Mn.79, Si.19, S.001, P.01, Cu.18, Ni.18, Cr.03	2.85	3.8	25	A – see above C D F	corr.	no	0.2N NaOH	810 1184 1434 1247	228 333 403 351	2.0	1.22 1.78 2.15 1.87
	Line pipe 5	C.09, Mn.77, Si.01,	1.73	3.8	25	C – see above	corr.	no	0.2N NaOH	1459	249	2.4	.95
		S.001, P.009, Cu.01 Ni.02, Cr.02				D E				2007 2356	343 402		1.13 1.35
	API ⁽⁴⁾ 5L- X65, TMPC	C.08, Mn 1.5, P .012, S .006, Si .27, Ni .02, Cr .02, Mo .00				pH 5.75: H2S sat g/L: seasalt 41.95, NaHCO ₃ 0.22				1339	204	0.45	4.8
	A516-70, hot rolled	C.21, Mn 1.12, P .011, S .017, Si .26, Ni .05, Cr .02, Mo .01	,			pH 5.50: H ₂ S sat g/L: sea salt 41.95, CH ₃ COOH 1.0.				1673	255	2.1	1.3
	A-516-70, low S, normalised	C.17, Mn 1.13, P .012, S .001, Si .26, Ni .05, Cr .02, Mo .01	,			pH 5.25: H ₂ S sat g/L: sea salt 41.95, CH ₃ COOH 0.2.				1391	212	1.3	1.7
	⁽⁴⁾ 5L-X52, hot rolled	C.08, Mn 1.18, P .014, S .013, Si .17, Ni .04, Cr .02 Mo .01	,			pH 5.00: H ₂ S sat g/L: seasalt 41.95.				2172	331	0.8	4.4
6	A516-70, Simulated	C.21, Mn 1.12, P .011, S .017, Si .26, Ni .05, Cr. 02, Mo. 01	15	*	27	PH 4.75: H ₂ S sat g/L: NaCl, 50, CH ₃ COOH 1, N ₂ OOCCH, 3H ₂ O, 5 1	corr	Pd	0.1N	2224	339	1.3	2.8
	A516-70, normalised	C.21, Mn 1.12, P .011, S .017, Si .26, Ni .05,	,	20	27	pH 4.75: H ₂ S sat g/L: NaCl, 50, CH ₃ COOH 1,	con.	Ĩŭ	NaOH	2730	416	1.4	3.1
	A841, ultralow S	C.13, Mn 1.10, P .007, S .001, Si .28, Ni .22	,			pH 4.00: H ₂ S sat g/L: NaCl. 50 CH ₂ COOH 10				6404	976	2.0	5.2
	adv. Steel, TMCP	Cr .01, Mo .01				NaOOCCH ₃ $3H_2O$ 5.1, NaOH 0.05							
	A106 Gd B, seemless	C.26, Mn 0.93, P .010 S .015, Si .28, Ni .04, Cr .03, Mo .02	,			pH 3.50: H ₂ S sat g/L: NaCl, 50, CH ₃ COOH 28.3, NaOOCCH ₃ 3H ₂ O 6.6.				3064	467	4.4	1.1
	A-516-70, HIC	C.17, Mn 1.09, P .01, S .001, Si .34, Ni .23,	1			pH 3.25: H ₂ S sat g/L: NaCl, 50, CH ₃ COOH 35.7.				5846	891	1.8	5.3
	resistant, normalised	Cr .06, Mo .07				NaOOCCH ₃ 3H ₂ O 5.1							

Continued on next page

Cor	ntinued from pre	evious page			Д	PPRC) \ ,	/F	-D				
ref	Steel	Composition	w/ mm	Area / cm ²	T∕ ℃	entry electrolyte	I _c / mA. cm ⁻²	Coat, µm	Exit electrolyte	Jss / pL cm ⁻¹ s ⁻¹	J.w / pL.cm ⁻¹ s ⁻	$\frac{10^{6} \text{D}}{\text{cm}^{2}}$	c ₀ / ppm
7	AISI ⁽³⁾ 410	As ref. 6	1 1	4.83	50 77	As ref. 4: 1000 ppm (wt) H_2S As ref. 4: 300 ppm (wt) H_2S	corr.	no	0.1N NaOH			0	.057 .091
8	20" line pipe	Mn 1.0, S .001	8.77	52	30	2 atm. H ₂ S	corr.	Ni	0.1N NaOH	2867	2481		~6
						15 atm. H ₂ S	corr.	Ni	0.1N NaOH	8477	7335		~11
9	Line pipe	Not specified	0.75	3.53	20	? pH 4.5, ref. 22, sat. H ₂ S	corr.	1 Pd	0.2N NaOH	6000	450		
			13					no	H2 Coll	1100	1430		
10	Ferritic steel	C.03,Si.2,Mn 1.2	3	3.4	20	pH 4.5, ref 22, sat. H ₂ S	.027	Ni	0.2N NaOH	2182	646	10.8	0.64
	with	+ Mo .15					.078	flash		4737	1402	7.5	2.00
	additions of	+ Cr3					.033	Pd		2967	878	7.9	1.19
	Mo, Cr, Ni	+ INI 3					.078			4027	1192	9.5	1.34
	orCu	+ Cu .5					.021			2867	849	8.6	0.96
11	High str. heat treat to 125 ksi	low alloy modified 4130 ⁽³⁾ chemistry	?	?	24	Various, 3% H ₂ S, 97% CO ₂	Corr.	Pd	0.1 M NaOH	4040	?	2.9	4.7
12	X65 linepipe			2	25	pH 5, 1 bar H ₂ S	Corr.	Ni	0.1 M NaOH	4160	417	-	-
			1			pH 4, 1 bar H ₂ S				4790	480		
						pH 2.5, 1 bar, H ₂ S				5670	568		
13	API ⁽⁴⁾ X65	C.09, Mn 1.56, Si .28,	10	45	25	pH 3.5, 3% H ₂ S, 97% CO ₂ , 5%	Corr	Pd	0.1 M NaOH	1764	1764	-	-
		P.014, S .001, Cr.05,	0.5	45	25	NaCl, 0.4% CH ₃ COONa	Com		0.1 M NaOH	3500	175	-	-
		Ni.03, Mo .01, Cu.02	0.5	45	25		Соп	по	H ₂ Collection		175	-	-
14	Structural	C.08, Si.34, Mn 1.1,	3	160	19	Ref 19, 0.4 atm. H ₂ S	Corr.	no	H_2	3745	1123	-	-
	carbon steel	P.01, S.004, Cr<.02,	6						collection	2291	1375		
		Ni.24, Cu.34, V .1	9	1						1554	1398		
			12							1146	1375		
	Plate 3	Please see Table 3	16	400	22	pH 4.5: ref 19, sat. H ₂ S @1	.099	no	H ₂	1030	1648	8.5	1.46
	Plate 5		16	400	22	bar, trial 3b	.115	no	collection	1075	1720	7.5	1.68

TABLE 3A. TRIAL PLATE STEEL CHEMICAL ANALYSIS

Plate, test	С	Si	Mn	Р	S	Cu	Ni	Cr	Mo	V	Ti	Nb	Al	Ν	B	Ca
3, Mill	0.18	0.37	1.14	0.013	0.005	0.03	0.04	0.22	0.02	0.007	0.004	0.017	0.035	-	0.0003	0.005
3, Exova ⁽⁵⁾	0.19	0.38	1.17	0.015	0.014*	0.03	0.04	0.21	0.02	0.008	0.004	0.015	0.040			
5, Mill	0.18	0.38	1.17	0.013	0.001	0.15	0.21	0.17	0.01	0.001	0.003	0.02	0.043	0.007	0.0002	0.0026
5, (5)	0.19	0.36	1.13	0.014	0.003*	0.17	0.22	0.17	0.03	-	-	-	0.050	-	-	-

* data obtained from Optical Emission Spectroscopy (OES) for which S readings are less dependable. A second crack susceptible plate, plate 4, was also used in initial trails.

TABLE 3B. PLATE PROPERTIES

Plate	Ana- lysis	0.2% PS, N/mm ²	0.5% Rt, N/mm ²	UTS, N/mm 2	% El	% RA
	Mill	371	374	540	28	N/A
3	(5)	385	388	555	35. 5	72
	Mill	N/A	396	554	33	N/A
5	(5)	405	403	565	34. 5	69

TABLE 4. SOLUTIONS USED IN TRIALS

trial	Solution	Details, comments
0	Ref. 19, Sol A, pH 2	5.0 wt % NaCl, 0.5 wt CH ₃ COOH. HCl to pH 2.0.
1,6	Ref. 19, Sol. A, pH 2.7 buffered	5.0 wt % NaCl, 0.5 wt%CH ₃ COOH buf (CH ₃ COONa)
2	Ref. 19, Sol. A, pH 2.7 unbuffered	5.0 wt % NaCl, 0.5 wt% CH ₃ COOH , unbuffered
3	Ref. 19, Sol. B, pH 4.5 buffered	5.0 wt % NaCl, 0.5 wt% acetic buffer
4	20% (NH ₄)HS, 0.1% NaCl, 1.25% KCN	20% (NH ₄)HS, 0.1% NaCl, 1.25% KCN
5	10% NH ₄ OH, KCN adn's	10% NH ₄ OH, KCN additions as identified

⁽³⁾ American Iron and Steel Institute.
 ⁽⁴⁾ American Petroleum Institute (API), 1220 L St. NW, Washington, DC 20005.
 ⁽⁵⁾ Exova Ltd, 182 Halesowen Rd, Netherton, Dudley, W. Midlands, UK

TABLE 5. SUMMARY TRIAL DATA

Tria	l Solut					Plate	e A da	nta							Pla	te B o	data					
	All saturated with 0.99 atmospheres H ₂ S	рН	purge	Plate	Cracks?	J (max)	Pre- sour corr. rate	max. corr. rate	delay	$D x 10^{6}$	c_0 initial	α	Plate	Cracks?	J (max)	Pre- sour corr. rate	max. corr. rate	delay	$D x I0^{6}$	c _o initial	ø	
			Hr			pl/cm ² /s	mm / yr	mm / yr	hr	cm^2/s	mdd	ppt			pl/ cm ² /s	mm / yr	mm / yr	hr	cm ² /s	mqq	ppt	
Ob	Ref. 19, Sol A, pH 2	2.0, unbuffered	-	3	×	634	Х	0.9	9.1	7.5	1.4 4	65	4	~	870	х	2.7	4.2	9	1.61		
0c	Ref. 19, Sol. A, pH 2	2.0 HCl addn. to maintain	-	3	×	1368	Х	Х	9	10	1.3 9	Х	4	~	965	Х	Х	2.3	12.5	1.28		
1a	Ref. 19, Sol. A (5% NaCl + 0.5% Acetic Acid)	2.7 buffered	46.3	3	×	1200	.664	2.45	14	10	1.5	45	5	~	1340	.338	2.76	22	x	x	45	
2a	Ref. 19, Sol. A	$2.7 \rightarrow 3.7$	5	3	×	1200	.62	1.31	17	12	1.2	84	5	~	1170	.49	1.75	7	7.5	2.2	61	
3b	Ref. 19, Sol. B	4.5 buffered	118	3	×	1030	0	1.15	8.8	8	1.5	82	5	~	1075	0	1.33	4.5	7.5	1.65	74	
4a	20% NH₄HS, 0.1% NaCl, 1.25% KCN	$9.9 \rightarrow 8.9$	168	3	×	842	0	2.38	x	х	X	32	5	~	936	0	2.27	x	x	x	38	
5a	10% NH ₄ OH, KCN additions	$12.2 \rightarrow 8.4$	29	(no ac	plate tually	A - to er positior	nable N ned at b	H4OH base of	add	itions, osion c	'Plat ham	e B' ber)	5	~	974	0	2.6	14.5	12	1.9	34	
6 a	Ref. 19, Sol. A	2.7 buffered	260	5	~	1085	х	2.42	4	10	1.4	41	5 - met	×	<3	Х	0.107	x	x	x	x	

TABLE 6. CRACK RATIOS

рН	Total H2 / 10 ⁹ pl/cm ²	Cracks	Aver	age		Sectio	on A		Section	on B		Section	n C	
			CLR %	CTR %	CSR %	CLR %	CTR%	CSR %	CLR %	CTR %	CSR %	CLR %	CTR %	CSR %
pH 2.7 non- buffered	0.445	Yes	67	8.5	1.13	59.1	6.23	0.8	91.7	14.7	1.9	49.2	4.63	0.69
pH 4.5 buffered	1.098	yes	107	9.4	8.11	103	7.2	7	108	12.1	11.7	109	8.83	5.64
	0.266	yes	64	5.8	1.27	74	5.67	1.42	47	3.33	0.98	71.3	8.43	1.41
pH 2.7 buffered	1.255	yes	110	20	8.56	102	19.8	11	126	20.5	3.41	101	20	11.3
				FIC	GURES			M	odelled flu	ux detail.	Trial 0b			-
	2 4 4 4 7 12 - 7					800								
	pH 2.7 non- buffered pH 4.5 buffered pH 2.7 buffered	pH Total H2 /10 ⁹ pl/cm ² pH 2.7 non- buffered 0.445 buffered 0.266 pH 2.7 1.255 buffered	pHTotal H2 / 10° pl/cm²CrackspH 2.7 non- buffered0.445YespH 4.51.098yesbuffered0.266yespH 2.71.255yesbuffered0.266yes	pHTotal H2 / 10° pl/cm²Cracks / AverpH 2.7 non- buffered0.445Yes67pH 4.51.098yes107buffered0.266yes64pH 2.71.255yes110buffered0107100pH 2.71.255yes107	pH Total H2 / 10 ⁹ pl/cm ² Cracks Average CLR CTR % CTR % CTR % pH 2.7 non- buffered 0.445 Yes 67 8.5 pH 4.5 1.098 yes 107 9.4 buffered 0.266 yes 64 5.8 pH 2.7 1.255 yes 110 20	pH Total H2 / 10 ⁹ pl/cm ² Cracks Average CLR CTR CSR % pH 2.7 non- buffered 0.445 Yes 67 8.5 1.13 pH 4.5 1.098 yes 107 9.4 8.11 buffered 0.266 yes 64 5.8 1.27 pH 2.7 1.255 yes 110 20 8.56 pH 2.7 1.255 yes 110 20 8.56	pH Total H2 / 10° pl/cm² Cracks Average Section PH 10^{9} pl/cm² Cracks CLR % CTR % CSR % CLR % pH 2.7 non- buffered 0.445 Yes 67 8.5 1.13 59.1 pH 4.5 1.098 yes 107 9.4 8.11 103 pH 4.5 1.098 yes 64 5.8 1.27 74 pH 2.7 1.255 yes 110 20 8.56 102 pH 2.7 1.255 yes 110 20 8.56 102 buffered 0.266 yes 110 20 8.56 102 pH 2.7 1.255 yes 110 20 8.56 102 buffered 5 5 5 5 5 80 40	pH Total H2 / 10° pl/cm ² Cracks Average Section A CLR CTR % CTR % CSR % CLR % CSR % CLR % CTR % pH 2.7 non- buffered 0.445 Yes 67 8.5 1.13 59.1 6.23 pH 4.5 buffered 1.098 yes 107 9.4 8.11 103 7.2 pH 2.7 non- buffered 0.266 yes 64 5.8 1.27 74 5.67 pH 2.7 1.255 yes 110 20 8.56 102 19.8 pH 2.7 1.255 yes 110 20 8.56 102 19.8 pH 2.7 1.255 yes 110 20 8.56 102 19.8 pH 2.7 1.255 yes 110 20 8.56 102 19.8 pH 2.7 1.255 yes 110 20 10.2 19.8 pH 2.7 1.25 yes 110 20 10.2 10.2 pH 3.5 yes 10.5 yes 10.5	pH Total H2 / 10^9 pl/cm ² Cracks Average Section A CLR CTR % CSR % CLR % CTR% % CSR % pH 2.7 non- buffered 0.445 Yes 67 8.5 1.13 59.1 6.23 0.8 pH 4.5 buffered 1.098 yes 107 9.4 8.11 103 7.2 7 pH 2.7 buffered 0.266 yes 64 5.8 1.27 74 5.67 1.42 pH 2.7 buffered 1.255 yes 110 20 8.56 102 19.8 11 pH 2.7 buffered 1.255 yes 110 20 8.56 102 19.8 11	pH Total H2 / 10^9 pl/cm ² Cracks Average Section Section Section Section pH CLR % CTR % CSR % CLR % CLR % <td< td=""><td>pH Total H2 /10° pl/cm² Cracks Averuge with the second s</td><td>pH Total H2 / 10° pl/cm² Cracks k Average k Section I Section</td><td>pH Total H2 / 10⁹ pl/cm² Cracks Cracks Average Series Section A Section B <</td><td>pH Total H2 /10° pl/cm² Cracks Average M Secion F Secio</td></td<>	pH Total H2 /10° pl/cm ² Cracks Averuge with the second s	pH Total H2 / 10° pl/cm ² Cracks k Average k Section I Section	pH Total H2 / 10 ⁹ pl/cm ² Cracks Cracks Average Series Section A Section B <	pH Total H2 /10° pl/cm² Cracks Average M Secion F Secio



FIGURE 1 - Experimental Apparatus Used in this Work



how delays in corrosion onset, t_{delay} are obtained







FIGURE 4 - Trial 0c. pH 2.7 with HCl additions. Dashed lines indicate HCl addition to maintain pH









FIGURE 8 - Trial 4a. pH 9.8, 20% NH₄SH, 0.1% NaCl, 1.25% KCN. Only spot measurements were observed and recorded. The continuous early data profile is reproduced from Trial 5a, Plate 5, offsetting the time such that *t* = 0 corresponds to KCN addition in that trial



FIGURE 9 - Trial 5a, pH 12.2 to 8.4, commence with 10% NH₄OH, pH 12.2



FIGURE 10 - Detail of trial 5 a after KCN addition

UNAPDO^\/CD



FIGURE 11 - Trial 6a, pH 2.7 buffered, one plate metalized

Coupon avg CSR vs total H2 collected from Plate 5, unmetallised



FIGURE 12 - Dependence of crack extent on total flux passed through wall



FIGURE 13 - a, *left:* A 65 mm wide section of the Trial 6a plate used (corroding face uppermost), showing two cracks. The plate CLR = 11.4%, CTR = 2.81%, CSR = 0.16%: much lower than the coupon from the same trial, b, *right*

a, Plate 3, x 50. UNAPPR b, Plate 3, x 200.



c, Plate 5, x 50, showing crack.







FIGURE 14 - Micrographs of plates used in the trials



FIGURE 15 - Modeled steady state flux obtained from Table 5 values and equation (2), plotted against corrosion rate 40 to 48 hr after sour injection, and model correlation line. Note pH 2.7 data is offset 0.5 mm/yr positively, corresponding approximately to the pre-sour corrosion rate

UNAPP¹**ROVED**



FIGURE 16 - Measured flux *vs* simultaneously determined LPR corrosion rate, at times t > 48 hr after sour exposure. Plate 5 trial 2a 'problem' data at t > 120 hr is encircled. Flux data from Laycock *et* al.¹⁰, Table 2, was normalized to 16 mm thickness for comparison



FIGURE 17 - Measured corrosion rest potential *vs* simultaneously determined LPR corrosion rate. Times *t* before or after onset of sour saturation are indicated

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