

THE EFFECT OF PRESSURE ON HYDROGEN CHARGING OF CARBON STEEL UNDER CATHODIC PROTECTION

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ABSTRACT

The mechanism of hydrogen uptake by steel in various environments is reviewed, in order to understand their propensity to cause hydrogen damage, as indicated by hydrogen entry activities at the steel subsurface. We then consider whether hydrogen damage is likely to be induced in cathodically protected steel, supported by new and previously published data. It is concluded that cathodic protection of steel in environments not containing hydrogen promoters such as sour gas probably generates hydrogen activities not exceeding ambient pressure. The hydrogen activity in the deep sea, at 400 bar, is considered low in comparison with activities commonly associated with sour environments, but it might induce cracking in an already highly hydrogen susceptible weldment, say. A mild charging solution is suggested to simulate the hydrogen charging activity induced by cathodic protection sub-sea.

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UNAPPROVED INTRODUCTION

There have been a number of reported failures of sub sea pipelines which have been under Cathodic Protection (CP). The general opinion has been that the hydrogen generated from the CP system has entered the steel and effectively caused Hydrogen Induced Stress Cracking (HISC)

Any hydrogen generated from the CP system would be evolved on the outside of the pipeline, where for instance the highest tensile stress from welding, and possibly the highest hardness areas would be located. Thus the three factors, normally required for cracking, are all present.

However, sea water is not normally associated with such damage. In particular, it is generally considered necessary for there to be hydrogen 'promoters' or 'occluders' specifically compounds, particularly the hydrides ¹, of As, Sb, P, S, Se, and Te as well as HF, to be present in an aqueous environment in order for such damage to occur. Concentrations of such species are normally miniscule in sea water, and they would not form upon the oxidation of steel under cathodic protection. It is recognised that some H₂S may be formed by the action of sulfate reducing bacteria, *thiobacillus ferrooexidans*, on steel in deep sea water, though this bacterial action is more generally observed in service steel containing sulfur rich petrochemical streams.

In the absence of occluders, the overwhelming proportion of hydrogen formed on steel under cathodic protection ultimately bubbles off at ambient pressure. Perhaps hydrogen damage is associated with the high pressures that prevail deep sea, typically 400 bar at 4000 m, the depth of the sea water remote from the continental shelves. A few authors²⁻⁶ have reported work simulating these conditions, and indeed some evidence of hydrogen damage in the laboratory has been presented. The point of this work is to consider whether at relatively low pressures (between 0 and 6 bar above atmospheric pressure) cause an increase in hydrogen flux through steel above what might be expected from a simple shift in reactions kinetics caused by the change in pressure.

REACTION KINETICS ASSOCIATED WITH HYDROGEN FORMATION ON STEEL

A proportion of hydrogen cathodically formed on a steel *entry* face during cathodic protection is liable to permeate through the steel and desorb as molecular hydrogen on the opposing, *exit* face. According to Fick's Law, the rate of flux is proportional to the concentration gradient, and over time, a uniform concentration gradient is established through the steel, with a uniform and invariant hydrogen flux entering and exiting the steel. It is useful to try and link the steady state flux to the rate of hydrogen entry, because the link between the two effectively links steady state hydrogen flux, J_s , with cathodic current i_c , according to equation (1) below.

The fate of hydrogen deposited on steel by cathodic reduction of protons is shown in Table 1. (Tables 2 and 3 provide flux and hydrogen concentration conversion figures which assist in converting between various units of measurement arising in this study). A clear distinction is made between surface hydrogen H_s , and hydrogen just under the surface H_s , because surface sites, that is, sites for hydrogen amenable to interfacial reactions, are probably very much more numerous and variant in energy than sub-surface sites. It is assumed that hydrogen exit reactions are rapid as compared with the hydrogen permeation, equation (5).

In order to obtain simple mathematical relationship between measurable parameters i_c (the impressed cathodic current), and J_s , we first make some bold assumptions, as summarised Table 1. We will see

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how these assumptions might affect experimental data fit later. For now, we note if reactions (2) and (3a) do not occur, then all the generated hydrogen enters the steel by reaction sequence (1), (5), (6), so $J_s = i_c$ and by conversion of molar equivalents we obtain 10,560 pL/cm²/s per mm/year corrosion. In fact this rarely happens. Hydrogen formed by reaction (1) substantially bubbles off at the steel entry face *via* reactions sequence (2),(5) or possibly (3),(5). In such cases hydrogen permeation (6) is the rate determining step for hydrogen permeation through steel. The relation $J_s = D.[H_0]/w$ is derived from Fick's Law, and supposes D is invariant for all c, which is an acceptable approximation, but not strictly so for typical steels¹, which will include a continuum of trap sites at grain boundaries, such as to cause steels to vary in diffusion coefficient by typically fifty fold at ambient temperatures⁷. The relation also supposes that the hydrogen exit sub-surface concentration $[H_w]$ is negligible as compared with $[H_0]$.

Now let us consider the steady state. All species will be at a time invariant concentration, including the entry face concentration of hydrogen, $[H_s]$. Hydrogen entry through steel will then be given by

$$J_s = \mathbf{D}.\mathbf{K}_5.[\mathbf{H}_s]/\mathbf{w} \tag{7}$$

Since at steady state the sum of rates of formation and removal of H_s will be zero, from (1), (2), (3a), (3b) and (6) we obtain:

+
$$I_{c1}$$
 + $k_{-3}[H_{2(ads)}]$ - $k_2[H_s] - k_3[H_s]^2 - D.K_4[H_s]/w = 0$ (8)

Equation (8) is a quadratic, the real root of which is:

$$[H_s] = \left[-(k_2 + D.K_4/w) + \left\{ (k_2 + D.K_4/w)^2 + 4(i_{c1} + k_{-3}[H_{2(ads)}]) k_3 \right\}^{1/2} \right] / 2k_3$$
(9)

From (7) and (9),

$$J_{s} = (D.K_{5}/w).[-(k_{2} + D.K_{4}/w) + \{(k_{2} + D.K_{4}/w)^{2} + 4(i_{c1} + k_{-3}[H_{2(ads)}])k_{3}\}^{1/2}] / 2k_{3}$$
(10)

A cumbersome equation. However, if we assume:

$$(k_2 + D.K_4/w)^2 \ll 4(i_{c1} + k_{-3}[H_{2(ads)}]).k_3$$
(11)

then (10) simplifies to:

$$J_{s} = D.K_{5}/w.\{(i_{c1} + k_{-3}[H_{2(ads)}]) / k_{3}\}^{1/2}$$
(12)

From (12) we would expect, in a given scenario, for the product of steady state flux and thickness, J_{sw} to be thickness invariant to a critical minimum thickness w at which the assumption (11) is invalidated. So is seen to be the case with literature data⁸⁻¹⁰ presented in Figure 1.

Supposing also that cathodic H formation (1) is the dominant cathodic reaction ($i_{c1} \approx i_c$), and that hydrogen dissociation (3b) is minor, then J_s will be proportional to the square root of cathodic current. this has been observed in preliminary work carried out by ourselves, Figure 2.

The effect of ambient pressure on hydrogen flux does not seem to have been systematically studied, but we can form a hypothesis. As pressure increases, desorption of molecular hydrogen by reaction (4) – in an early stage of bubble nucleation - will be retarded. By this means, even in the absence of occluder, when the equilibrium constant K₅ is low, we expect the adsorbed hydrogen concentration [H_{2(ads)}] to increase with ambient pressure according to (12). Specifically, at equilibrium, the maximum hydrogen

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concentration on the surface of ambient pressure *p* bar will have a fugacity (gaseous activity) of *p* bar. In turn, the maximum activity of hydrogen formed on the surface by dissociation of this hydrogen, $a(H_s)$ will be $p^{1/2}$ bar^{1/2}. Note the square root arises from Sievert's Law. For the equilibrium (3a)/(3b), $K_3 = k_3 / k_{-3} = [H_{2(ads)}]/[H_s]^2$ so $[H_s] = ([H_{2(ads)}]/K)^{1/2}$.

Through equilibrium (5) we would then expect the steel sub-surface hydrogen H₀ to be at an activity, $a(H_0)$, which we signify $a_0 (bar^{1/2})$ of $p^{1/2}$. On this basis, we would expect in 4000 m seawater, where the pressure is 400 bar, the activity $a_0 = 20 bar^{1/2}$.

LINKING FLUX AND AMBIENT PRESSURE: SURFACE HYDROGEN ACTIVITIES AND HYDROGEN CRACKING PROPENSITY.

As suggested above, it is possible to attribute hydrogen activities, $(a_0)^2$ to various hydrogen charging scenarios. In effect $(a_0)^2$ is the pressure in bar of gaseous hydrogen that would be at equilibrium with the atomic hydrogen at the concentration just under a steel surface caused by a charging particular scenario To a first approximation activity is independent of the steel's behaviour to hydrogen – solubility, diffusivity, cracking susceptibility and so on – and simply indicates the hydrogen charging severity of the process.

The permeability P (Ncm³.cm⁻².s⁻¹ cm.bar^{-1/2}) of hydrogen through steel is defined by:

$$J_{\rm s} = \mathbf{P}. \, \boldsymbol{a}_0 \,/\, \boldsymbol{w} \tag{13}$$

P is the product of hydrogen solubility S (Ncm³.cm⁻³.bar^{-1/2}) and diffusivity D (cm².s⁻¹); hydrogen permeability depends on how much hydrogen enters steel and how fast it moves through the steel. Since D and S vary exponentially with temperature T (deg Kelvin), so does P:

$$P = P_0. \exp(-E_a / RT)$$
⁽¹⁴⁾

 P_0 is a pre-exponential factor, R the gas constant and E_a an activation energy. Grabke and Reicke⁷ point out for mild steels P does not vary significantly, in so far as the presence of elements which increase hydrogen trapping cause solubility S increase, and diffusivity D to decrease, in the same proportion. We adopt their values for Q and T steel; $P_0 = 0.00187$, and $E_a = 4126$ kJ/mol.

Using (13) and (14) we can estimate activities from flux data, and *visa versa*. Table 4 offers some illustrative sub-surface hydrogen activities, that have been derived in this way. Several insights are to be drawn. Firstly, permeability is very temperature variant, and a robust flux can be obtained from acidic corrosion, even if the corrodant is not a hydrogen promoter, and only generates around a bar of hydrogen activity. Indeed, the reason that hydrogen damage is seldom observed above 100 °C is that virtually no scenario injects sufficient hydrogen to cause cracking. From flux obtained from NACE solutions we obtain activities exceeding 2,000,000 bar equivalent, which, interestingly, is approximately the Young's modulus for carbon steel. Much lower activities are obtained from cathodic studies, such as our own, now presented.

EXPERIMENTAL METHOD

Apparatus used to evaluate the effect of pressure on cathodically protected steel is shown in Figure 3, comprising carbon steel pipe of wall thickness 6 mm, sealed at the top and bottom with steel plates of



10 mm thickness and a gasket of 4 mm thickness. Bulkhead compression fittings^a were used to connect ¹/₄ inch outer diameter copper gas lines to electrodes through the steel plate. A leak-proof vessel capable of sustaining pressures to at least 10 bar was assured with 10 mm diameter studs. Hydrogen^b was admitted through a gas bubbler in the enclosure to maintain a purge of the solution and regulate pressure and was also utilised as a purge.

The steel pipe itself formed the cathode. Platinum foil and mesh, were used as reference and counter electrodes, the latter being of several square centimeters area.

The buffered electrolyte solution consisted of 0.5% wt. acetic acid, 2% wt sodium acetate, 5% wt sodium chloride, the rest being de-ionised water and having a pH of 5.1.

Constant current was supplied using a galvanostat manufactured in-house. The hydrogen pressure was measured using an analogue gauge^c while the hydrogen flux was measured by the hydrogen collection method^d The current and voltage potentials were measured with multimeters^e.

Before each trial the inner surface of the pipe was ground to a P600 finish with SiC paper. The enclosure was assembled and any leaks eliminated by using pressurising the enclosure with 6 bar hydrogen. Two liters of pre-hydrogen purged electrolyte solution were then siphoned into the enclosure, and the solution repurged using the internal gas bubbler. The solution was then subjected to cathodic currents of up to 0.5 mA/cm^2 and pressures of up to 6 bar hydrogen. Hydrogen flux, and potentials of electrodes relative to the steel pipe, as well as the applied current, were routinely monitored.

During operation, the ambient temperature was maintained between 17 and 19 °C. Variance in pressure due to atmospheric changes was +-0.15 bar.

RESULTS AND DISCUSSION

The last two rows of Table 3 were obtained from measurements at pressures typical of the deep sea. It is clear from the table that some well known hydrogen activities associated with hydrogen damage greatly exceed 400 bar, the pressure of deep sea water. As can be seen, de Luccia data² indicates hydrogen activities considerably in excess of the ambient pressure. Supposing his readings are correct, a possible rationale is as follows. We know that in studies of flux *versus* applied cathodic current *i* in the presence of hydrogen promoters, there is a linear relationship between J_s and $i^{1/2}$. Kinetically, this requires hydrogen association at a steel surface to proceed *via* migration of surface hydrogen atoms H_s, reaction (3a).

The low temperatures (4 $^{\circ}$ C) of a deep sea environment are expected to not only retard this H_s migration, but also migrating H_s at a lower temperature would have less thermal energy to displace adsorbed molecular hydrogen H_{2(ads)}, expected to be more populous on the steel at the prevailing pressure of 400 bar. Thereby an activity greater than 400 bar in deep sea environments is feasible. However, the deLuccia data is not supported by other work. In particular, flux is expected to increase linearly, not with the square root, of applied pressure, as we expect. Also, conducting experiments with hundreds of bar of hydrogen pressure delivered across a 1 mm steel Devanathan cell membrane, hydrogen leakage could be an issue, and the experiments were also conducted at pH 1, so the formation

^d Hydrosteel 6000, Ion Science Ltd.

^a Wade

^b 99.99%, Air Products

^c RS components, 405-5593

^e Caltek CM1200C

of hydrogen occluding species at the steel entry side is certainly plausible, if an insufficient cathodic bias was not applied at all times.

Notwithstanding, the maximum hydrogen flux obtained from this work in the absence of a hydrogen occluder is shown in Figure 4, approximately 1.5 pL/cm²/s, obtained at p = 6.5 bar and $i_c = 0.2$ mA.cm⁻². From equations (13) and (14) we obtain a value for the entry sub-surface hydrogen activity a_0 of about 0.7 bar. We observed a similar increase in flux and activity was observed with a pH 4 solution, containing 2 g/litre sodium sulfide, upon increasing the purge pressure from 1 to 6.5 bar. We conclude that at pressures of a few bar there is no appreciable affect of increased pressure on hydrogen entry above what might be expected due to shift in surface reaction equilibria due to retarded bubble nucleation, discussed above. Woodward *et al.* data³ also indicate an activity comparable to ambient pressure, Table 4.

Hydrogen damage susceptibility is very dependent upon residual stresses and local hardening. In a weld, conditions may conspire to cause a hydrogen activity limit for cracking of only 400 bar, to be expected from an appropriate shift of equilibrium (3) to the left . It should be noted that once a crack has initiated, crack propagation requires much lower hydrogen activities than those presented in Table 4 for hydrogen cracking associated with sour corrosion.

Although Pohjanne *et al.*⁴ do not provide flux data, they report slight indications of cracking and associated hydrogen uptake in duplex steel under cathodic protection and high hydrostatic pressures. Further, it is evident from work by Festy *et al.*^{5,6} that high hydrostatic pressures increase crack propagation, and shorten time to failure of steels under a given stress intensity. As compared with room temperature, a deep sea temperature of 4 °C will also increase crack susceptibility of a given steel in so far as this will increase stress and decrease hydrogen solubility in the steel.

To summarise, on the basis of our present understanding we would suggest that the prevailing deep sea water pressure is like to retard molecular hydrogen desorption on steel, increasing hydrogen activity at the steel surface to that of the environment.

A HYDROGEN CHARGING ENVIRONMENT SIMULATING CATHODIC CHARGING OF STEEL AT 400 BAR

An appropriate charging environment simulating conditions on the deep sea is established as follows. Firstly, we state the objective as finding a hydrogen occluding environment which generates a hydrogen activity a_0^2 of 400 bar, or $a_0 = 20$ bar^{1/2}

We obtain from Table 3 an activity a_0^2 generated by 1 bar H₂S at pH 2 in NACE A solution of about 2.5 million bar, for which therefore $a_0 = 1580$ bar^{1/2}. Now, like any other hydrogen occluder, the effect of H₂S is that of a surface catalyst. For example, adsorbed conjugate base HS⁻ may be involved in a concerted cathodic reaction such as (15):

$$(Surface) - Fe-S-H + H^+ + e = Fe-S-H + H(in Fe)$$
(15)

One **H** is in bold face to indicate the identity of the dissolved atom. Note H on S is anticipated not to migrate freely and associate, as is expected of H_s *ie*, (Fe-H) according to reaction (3a) above. What makes this particular mechanism so attractive is that it requires the conjugate base to contain hydrogen. All hydrogen promoters contain one hydrogen in their conjugate base, even HF_2^- . Therefore we expect

flux associated with hydrogen entry to increase proportionately to the concentration of adsorbed HS⁻. Experimentally, the relationship determined is probably J_s proprotional to $p(H_2S)^{0.25}$.¹²

Now, since J_s increases in proportion with a_0 , equation (13), we also expect a_0 to increase as $p(H_2S)^{0.25}$. The pressure of H₂S required is therefore mimiscule $[(20/1580)^4 = 2.6 \ 10^{-8} \text{ bar}]$. Clearly such low partial pressures of a corrodant cannot be reliably generated, and a less hydrogen occluding species is needed to simulate the effect of pressure on cathodically protected steel in the deap sea. Other matters to consider are the increase in solubility of occluders at decreasing temperature (about 5900 *vs* 3900 ppm for H₂S at 4 vs 20 °C)¹³, and that a steel's susceptibility to cracking, as measured by a critical activity a_0 , might be halved by the typical 2-fold decreased solubility⁷ of hydrogen in steel at 4 vs 20 °C.

Any simulating tests should be carried out according to established procedures and solution A conditions decreed in NACE TM0177, at a sufficiently low pH for sulfide scale formation not to be an issue.

CONCLUSIONS

Consideration of literature data and a model for hydrogen reactions on and in steel led to a view that hydrogen association primarily proceeds *via* the surface reaction $2H_s \rightarrow H_{2(ads)}$ and that hydrogen occluders retard this reaction. Test steel should be at least 5 mm thick, applied current less than 1 mA/cm² and plenty of time allowed for trap filling at low permeation rates. A trial at pH 5.1, under 6.7 bar hydrogen pressure and subject to 0.2 mA/cm² cathodic current delivered after four days a hydrogen flux corresponding to a low entry sub-surface hydrogen activity of less than a bar.

Further, cathodic charging at the prevailing pressure of 400 bar is expected to lead to an increase in hydrogen activity in the steel sub-surface to about 400 bar equivalent, sufficient to crack very susceptible weldments or cause pre-existing micro-cracks to grow. It is also feasible that hydrogen promoters (possibly H_2S derived from sulfate reducing bacteria) in conjunction with high i_c might promote sufficient hydrogen activity to cause hydrogen induced cracking in deep sea environments. Finally, it was considered that the deep sea environment cannot be approximately simulated by using NACE TM0177-Solution A with hydrogen sulfide, as it is too strong a hydrogen promoting catalyst.



UNAPPROVED TABLES

TABLE 1 - Representative flyurogen reactions associated with steel under flyurogen protect

Reaction	no.	Description	assumptions	rate of reaction:	
$H^{+}_{aq} + e \rightarrow H_{s}$	(1)	Cathodic H formation	irreversible.	i_{c1}	
H^+_{aq} +e + $H_s \rightarrow H_{2(ads)}$	(2)	Cathodic H ₂ formation	irrev., all H _s equivalent	$i_{c2} = k_2[H_s]$	
$H_s + H_s \rightarrow H_{2(ads)}$	(3a)	Surface H ₂ association	all H _s equivalent	$k_3[\mathrm{H_s}]^2$	
$H_{2(ads)} \rightarrow H_s + H_s$	(3b)	Surface H ₂ dissociation	all H ₂ equivalent	$k_{-3}[H_{2(ads)}]$	
$H_{2(ads)} \rightarrow H_{2 \ (gas)}$	(4)	Hydrogen desorption	very fast	$\{= rate of (2)+(3)\}$	
$H_s \leftrightarrow H_0$	(5)	Hydrogen sub-surface entry	equilibrated	$[H_0] = K_5.[H_s]$	
$H_0 \rightarrow H_w$	(6)	Hydrogen permeation	D invariant, no trapping, $H_w \ll H_0$	$J_s = D.[H_0]/w$	

^{a)} k_x = forward rate constant for reaction x. H_w is exit sub-surface hydrogen, through steel of thickness w, akin to H_0 . Note the reaction $H_0 + H_s \rightarrow H_{2(ads)}$ is excluded as being not being a significant determinant of hydrogen occlusion, as statistically, at least two thirds of hydrogen entering the steel sub-surface by representative reaction (5) will not return.

IADLE 2- Flux Unit Conversion							
10 ⁻⁶ mol H ₂ .cm ⁻² .day ⁻¹	1 pL.cm ⁻² .s ⁻¹	1 μA.cm ⁻²	10 ⁻¹² mol H.cm ⁻² .s ⁻¹	10 ⁻⁹ Ncm ³ .cm ⁻² .s ⁻¹			
=	=	=	=	=			
1	0.00359	0.448	0.0432	0.00381	10 ⁻⁶ mol H ₂ .cm ⁻² .day ⁻¹		
278.42	1	124.66	12.03	1.0594	pL.cm ⁻² .s ⁻¹		
2.23	0.00802	1	0.0965	0.0085	μ A .cm ⁻²		
23.15	0.0831	10.36	1	0.0881	x10 ⁻¹² mol H.cm ⁻² .s ⁻¹		
262.79	0.94	117.66	11.35	1	x 10 ⁻⁹ Ncm ³ .cm ⁻² .s ⁻¹		

TABLE 2- Flux Unit Conversion^{a)}

^{a)} pL quoted at 20 °C, 1 bar. Ncm³ are at 0 °C and 1 bar.

		0			
	1 µmol H.cm ⁻³	10 ¹⁸ atoms .cm ⁻³	1 Ncm ³ .cm ⁻³	1 ml.(100 g) ⁻¹	1 ppm by wt
	=	=	=	=	=
ppm by wt	0.127	0.211	11.21	0.82	1
ml.(100 g) ⁻¹	0.156	0.259	13.7	1	1.225
Ncm ³ .cm ⁻³	0.0114	0.0189	1	0.0728	0.0892
x 10 ¹⁸ atoms.cm ⁻³	0.602	1	53.0	3.86	4.73
µmol H.cm ⁻³	1	1.661	88.1	6.410	7.86

TABLE 3 - Hydrogen in steel concentration

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Evnt	a_0^2 / bar	Comments
Daf		Comments
Rel.	П2	
11	9,100,000	20" dia 8.7mm wall line pipe. Mn 1.0. Ni
		flash Devanathan Cell.
8	2,500,000	16 mm A516 steel,
		H collection method
	2200	Lower threshold defining sour service
	40,000	Assumes no deep traps, and solubility of
		mobile H in steel at 20 °C = 5 ppb per bar ^{1/2}
	6500	Dependent on scale and co-corrodants
		-
	0.5	Limited data
	2,000,000	= 200 GPa
2	39,000	0.96 mm, Armco iron, Pd coat Dev., pH 1
3	56	0.5 mm, Pd coat, art. sea-w, Dev. Cell
	Expt Ref. 11 8 2 3	Expt a_0^- / bar Ref. H2 11 9,100,000 8 2,500,000 2 2200 40,000 6500 0.5 0.5 2,000,000 2 2 39,000 3 56

TABLE 4 - Hydrogen	Activities as	ssociated with	typical flux	associated	with certa	in scenarios ^{a)}
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^{a)} calculated from permeabilities Where known, experimental sources of flux scenarios are quoted. Other activities are based on flux estimated from unpublished data.





FIGURE 1. Dependency of flux x thickness on thickness for sour saturated solutions at 1 bar (corrosion 1.6 mm/yr from current $i_c = 0.135 \text{ mA/cm}^2$), and 0.4 bar for comparison with Dean data⁸, which like Bonis and Crolet 2002 data⁹ used the hydrogen collection method and complied fairly well to the model trend. Both model lines use the set of kinetic constants for cathodic H₂ formation in Figure 2. Hay 1991¹⁰ shows the trends despite measurements upon the different steels. This, and other isolated data employing the Devanathan cell with 1 bar sour saturated solutions tends to fall below the 1 bar model.



FIGURE 2. Flux-thickness vs $i^{1.2}$ plots on 2 mm thick mild steel, showing linear region and in case of pH 6.8 solution, a flux maximum indicating the limited vacancies available for hydrogen on a steel surface.



FIGURE 3. Schematic representation and photograph of experimental apparatus.



FIGURE 4. Small but just measurable flux of some 1.5 pL/cm2/s obtained after 72 hr at $p(H_2) = 6.7$ bar, $i_c = 0.2 \text{ mA/cm}^2$. Before impressing current, $V_{\text{Ref 1}} = V_{\text{Ref 2}} = 0.09 \text{ V}$ vs cathodically charged steel. After 72 hr, $V_{\text{Ref 1}} = 0.08 \text{ V}$, $V_{\text{Ref 2}} = 0.09 \text{ V}$.

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