

APPLICATIONS OF HYDROGEN FLUX MONITORING TO PRE-WELD BAKEOUTS OF STEEL

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ABSTRACT

During a pre-weld bakeout, hydrogen efflux was monitored in real time using the hydrogen collection method at high temperatures. A circular section of a 50 mm thickness alkylolation unit acid storage vessel dome which had developed severe hydrogen blistering was removed, and pre-weld bake-out applied using heat pads placed within twelve inches of the cut-away section perimeter, on the dome's exterior face. A ring of eight hydrogen collection probes were placed under the heat pads, about six inches from the cut-away perimeter. One probe became blocked and failed to deliver measurement. The remaining seven delivered flux values indicating effective bake-out at five sites, and the need for extended bake-out at two neighbouring sites. The efflux trend at these sites strongly indicated initially high concentrations of hydrogen liberated by the bake-out. Corresponding efflux measurements at corresponding positions on the dome's interior face were much lower. A model of hydrogen diffusion for the bake-out, incorporating a high density of trapping sites located at depths of 5-15 mm beneath the monitored exterior face provided model flux transients consistent with field flux transients and spot measurements. The work demonstrated that pre-weld heat treatment can be assessed, extended or reduced in real time, on evidence provided by spot high temperature hydrogen efflux measurements at a small number of sites. An additional bake-out is presented in which near zero hydrogen effluxed.

INTRODUCTION

Pre-weld hydrogen bake-outs are considered a necessary measure in the elimination of hydrogen from steel which has been subject to uptake of diffusible hydrogen during

previous service. Hydrogen uptake by steel, and diffusion through it, occurs at low temperatures as a result of corrosion involving hydrogen promoters, such as H₂S and hydrofluoric acid, or at high temperatures due to naphthenic acid corrosion, or dissolution of molecular hydrogen in service, or, indeed, from the uptake of hydrogen from any source of hydrogen during manufacture. A substantial proportion of diffusible hydrogen is trapped within the steel, particularly by non-ferrous inclusions. In scenarios of severe hydrogen charging, hydrogen activities within steel can exceed 10⁵ bar, and hydrogen forms micro and macro blisters which may also retain substantial quantities of hydrogen over extended periods of time, as well as new trap sites associated with non-ferrous inclusions.

Trapped hydrogen presents a risk to welding arising from the large temperature gradients prevailing within a weld. Thermal energy releases hydrogen from traps. The hydrogen then migrates to a region of higher temperature (ie, towards the weld pool) on account of hydrogen's substantially increased solubility and increased diffusivity at increased temperatures. The escape of weldment hydrogen into the adjoining metal and the atmosphere is slow in comparison with its rate of cooling, particularly for weldments of more than 25-30 mm thick. Consequently, within one or two hours of welding, a large weldment can contain hydrogen at concentrations far exceeding its low solubility at ambient temperatures, leading to stress oriented hydrogen induced cracking^{1,2}.

The measurement of hydrogen permeation or *flux* (flow per unit area) through steel has been used to monitor corrosion due to sour gas (H₂S), hydrofluoric acid, and more recently, naphthenic acid corrosion at elevated temperatures (300-400 °C)³. A reliable and effective non-intrusive flux measurement tool operating at these temperatures is also attractive in bake-out monitoring, because it is completely non-destructive, and a measured flux of hydrogen emanating from a steel surface, J (pl.cm⁻².s⁻¹) summed over elapsed time t (s), can be directly equated with the concentration of hydrogen in steel c (parts per million by weight, or ppm), released from a depth x beneath the detector surface:

$$c = K / x \int J . dt \quad (1)$$

where K is the appropriate conversion factor, equal to 10.39 ppm per pl.cm⁻² effluxed. Diffusible hydrogen concentrations prevailing in welds themselves and in manufactured and milled steel have also been assessed by this technique.

In recent years the hydrogen collection method, has been developed and presented⁴⁻⁷ which appears to offer extremely sensitive (± 1 pl/cm²/s), rapid (60 s) and reliable (+/- 10%) measurement of hydrogen efflux from steel over a wide range of steel curvature (down to 2" diameter piping) and surface temperature (up to at least 350 °C^{3,6}).

This work concerned a laminated area of plate on the top dome of the acid storage vessel highlighted during a scheduled inspection in 1999. The laminated area consisted of many

small segregations and inclusions. Two hydrogen blisters were visible in the centre of the laminated area of plate, as shown in **Figure 1**.

Laminations that are parallel to the plate surface are not detrimental, unless they are in a hydrogen charging environment and are in close proximity to structural discontinuities, such as a weld. In this case, migration of diffusible hydrogen to the laminated area, and formation of molecular hydrogen at inclusions had caused the blisters to form and grow, as monitored by 100% manual ultrasonic test method (USTM) supported by time of flight diffraction (TOFD). Detailed corrosion mapping was also carried out to give a pictorial, two-dimensional view of the region¹. It was further deemed necessary to carry out TOFD/USTM inspection on the interior surface of the top head to establish the true condition of the material below the blisters. In this case the blisters had, unusually, formed only 5 to 15 mm from the outer surface of the 50 mm thick plate, suggesting the material below was relatively defect free. The relatively thin ligament of material above the blisters enabled them to grow at a much higher rate than would normally be expected, as indicated in **Figure 2**.

Internal inspection confirmed the presence of a light fluoride scale (FeF_2), which is itself the result of a corrosive reaction $2\text{HF} + \text{Fe} = \text{FeF}_2 + 2\text{H}$. There was no evidence of significant corrosion in the vessel by USTM inspection. Apart from the illustrated area of laminated plate, only isolated inclusions/laminations were identified elsewhere on the vessel.

A thorough technical review was carried out. The review included a fitness for service assessment based on API579, BS7910 and Serviceability of Petroleum Process and Power Equipment ASME 1992, fitness for service assessment procedure for Hydrogen blisters. Design code minimum wall thickness was calculated at 38mm (38mm + 3.2mm corrosion allowance) Actual wall thickness = 50mm. The extra material thickness is required at the knuckle region, where additional stress and load is induced due to supporting the acid settler vessel above. The vessel was deemed fit for service, but a means of preventing further growth of the lamination/blisters was required.

Various repair options were considered. It was agreed to drill the blisters. A method statement was formulated and subsequently risk assessed. Following the successful drilling of the blisters, as a precautionary measure TOFD inspection was carried out on the inside surface to confirm the features of the laminations had not changed significantly. This also allowed a footprint of the area to be obtained for future reference.

It had been considered that by drilling the blisters, and allowing the area below the blisters to vent, further blister growth might be prevented, or at least retarded. As the area of hydrogen damaged plate increased in size significantly following the release of the hydrogen from the blisters, and as the growth was towards a circular weld, it was deemed necessary to remove the damaged area. This required a further Engineering review to determine the best method of repair. It was decided to remove a circular cut away section. Due to the service and proximity of damage, a hydrogen bakeout of the cut-

¹ Andscan ®, Agfa Corporation

a way perimeter was considered essential prior to welding of the replacement section. The need for, and progress of, the hydrogen bakeout was evaluated by flux monitoring.

PROCEDURE

A circular cutaway was removed as demarcated in **Figure 1**, and illustrated in **Figure 3**. The bakeout zone was located within twelve inches of the 1.2 m diameter cut-away section perimeter, as shown in **Figure 3b** on the dome's external face ⁽¹⁾. Initially thermocouple wires were attached to the vessel as shown. Heat-pads were located at the indicated positions, together with eight flux collection probes, as discussed below.

Insulation was placed over the heated zone. Heat input was limited to 200⁰C per hour. Outgas temperature was 308 ± 8 ⁰C, maintained for a minimum of 2 hrs per inch of wall thickness (4+ hrs) This was extended to 8 hrs (2 x 4 hrs) following a review of the hydrogen permeation rates, as discussed hereunder.

Throughout this work an intrinsically safe hydrogen collection tool ⁽²⁾ was used to obtain efflux data³⁻¹¹. In brief, a collector probe, **Figure 4**, comprising a flexible steel plate 'collector' is attached by straps, banding or magnetically to a steel surface of variable curvature. The underside of the collector had a raised spiral ridge and central capillary such that air drawn into the capillary was first caused to sweep over the steel surface, entraining any emanating hydrogen. From the capillary the air stream is drawn through a flexible capillary, across the sensing face of a detector, and thence to a low voltage, pneumatic pump. The detector current is amplified and displayed or stored. The measurements provided by the hydrogen collection tool are described in more detail elsewhere³⁻⁷. For low temperature (<150 °C, 300 °F) steel surfaces, a 140 mm diameter probe illustrated in **Figure 4a** was used. The low temperature probe was manipulated with the central handle and the magnets sewn into a leather 'collector bracket'. The probe also contained a strap to facilitate attachment to piping of diameter < 8". This probe was used to measure flux following the discovery of hydrogen damage, and immediately before the bakeout.

During the bakeout, probes tolerating high steel surface temperatures (<450 °C, 840 °F) of 57 mm diameter, shown in **Figure 4b**, were positioned under the lips of adjacent heat-pads as shown schematically in **Figure 5**. A roaming high temperature probe, **Figure 4c** was used once during the bakeout to obtain flux readings from the cutaway perimeter interior face. Extensive readings from the vessel underside were limited for safety reasons. Flux readings were obtained from probes either by continuous monitoring and by sequential 60 s 'spot' measurements of hydrogen flux. Throughout the evaluation the prevailing hydrogen background in air was routinely monitored, and found to remain less than 50 pl/cm²/s equivalent.

⁽¹⁾ The bakeout installation and control was carried out by Specialist Heat Services, Swansea, UK

⁽²⁾ Hydrosteel™ 6000 analyser, attached to low and high temperature roaming probes Hydrosteel LT-R, and HT-R, marketed and manufactured by Ion Science Ltd, England

RESULTS

Twelve months after the blisters were identified, flux was monitored at sites on, and bordering, the blister field shown in **Figure 2**. Spot flux values can be related to the entry hydrogen activity a_o ($\text{bar}^{1/2}$) according to equation (2), derived in reference 3,

$$a_o = 0.0003534 J_{ss} \cdot w \cdot \exp(3586/T) \quad (2)$$

where J_{ss} is the steady state flux ($\text{pl}/\text{cm}^2/\text{s}$), w the steel thickness (cm) and T the steel temperature (K). We note that $(a_o)^2$ corresponds to an equivalent molecular hydrogen gas pressure at the corroding face in units of bar. The dome steel tested in this work was at approximately 300 K, and 5 cm thick. The time required for a steady state J_{ss} to be established in this case in response to a step change in a_o is about 2 months! However, activity flux in the HF service environment can be fairly invariant over this time scale. From (ii) we derive from the maximum efflux value of $70 \text{ pl}/\text{cm}^2/\text{s}$ a hydrogen activity of 40,000 bar approximately averaged over the time scale of establishing steady state, namely 2 months. Again, it should be noted that this activity is not untypical of HF service equipment, as determined in surveys of several HF Alkylation units.

Generic experience with flux associated with steel cracking leads us to believe that the quality service steel would be at risk from HIC nucleation at an activity of several hundred thousand bar, and a severe hydrogen episode may have led to these conditions prior to the steel damage being identified. However 40,000 bar is deemed sufficient to cause blister *growth* at an average depth of 10 mm from the exit (exterior) steel surface: the activity at this depth at an entry activity of 40,000 bar is calculated as $10/50 \times 40,000 = 8000$ bar. Of course, it is unlikely that sizeable blisters would sustain this pressure; as they grew the pressure within them would drop to much lower values. The low flux readings recorded *on* the blisters, typically 0 to $2 \text{ pl}/\text{cm}^2/\text{s}$, at a blister depth of 10 mm, corresponds to a blister hydrogen activity of less than 2 bar. It should be noted that a loss in activity would have resulted from low temperature, rate-determined hydrogen solubilisation at blister walls, so this is probably an underestimate of actual blister pressure.

The flux readings of the bake-out itself are illustrated in **Figure 6**. Immediately striking is the magnitude of flux registered, particularly given that it had been out of service for at least 12 months. By way of comparison, three equidistal circumferential sites located at a vertical mid-section of a 3 m column were fitted with probes exactly as described above. An identical bake-out temperature cycle was used on the 50 mm steel, previously subject 70°C high pressure hydrogen service. The results are shown in **Figure 7**, indicating maximum flux of $150 \text{ pl}/\text{cm}^2/\text{s}$, less than 1% of corresponding values obtained from the acid storage vessel bakeout. For further comparison, a survey of typical 40 mm steel plate exiting a steel plate mill at 300°C rarely exhibited flux $>1000 \text{ pl}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$.

Figure 6 shows that the ranking of site B to H spot measurements by flux magnitude at any one time scarcely changed throughout the bake-out. Thus, any single spot measurement, secured some time after maximum steel temperature was attained,

provided a good indication of remaining diffusible hydrogen in the steel under that location and temperature.

From equation (i) we obtain maximum total hydrogen out-gassed at respective bakeout sites, illustrated in **Figure 8**, expressed as $c \cdot x$; the average hydrogen in steel concentration released, c (ppm), to a depth of steel, x (cm). Whilst these levels may appear modest, it should be recalled that equation (i) assumes all hydrogen escape is directed normal to the steel surface. Since the diffusion parallel to the steel surface is enhanced with respect to normal diffusion (due to elongation of grains parallel to the surface during plate manufacture and therefore less intergranular hydrogen migrations per unit distance in this direction) the estimates are low: substantive hydrogen could be expected to diffuse towards and efflux from the cut-away perimeter. The high and slowly decaying efflux from sites G and H therefore led us to conclude that a further bakeout at 310 °C was warranted, and on the day following the work carried out by site staff. Initially, zero flux was reported at site H. On reaching 320 °C, the flux returned to its final value shown in **Figure 6**, namely 13,000 pl.cm⁻².s⁻¹, decaying slowly for two hours, then more abruptly, reaching less than 500 pl.cm⁻².s⁻¹ after 4 hr. At this point the bakeout was deemed complete.

The high concentrations of hydrogen collected from sites G and H corresponds to those sites being closest to the areas of lamination and blistering in the steel cut away, as indicated in **Figure 8**. Perhaps even more significant, this is precisely the direction in which the field of hydrogen lamination had been growing, **Figure 2**, whereas extensive USTM and TOFD scanning failed to identify damage outside the cutaway perimeter. On the evidence of this we are convinced that, presented with high hydrogen activities, substantial densities of hydrogen traps are generated in steel, wherein permanent hydrogen uptake occurs, prior to their development into detectable laminations and blisters.

Several flux profiles shown in **Figure 6** show striking peaks which invite attempts to explain the profiles in terms of a model, which could be further used predictively in future bake-outs of this type. Before presenting our initial investigations in this area it is worth stating that the rate of escape of hydrogen from a steel surface *is* the hydrogen flux J , and equation (i) from which **Figure 8** was obtained, presents a powerful first line of approach in the field for determining the concentration of hydrogen emanating from steel, and concentration liable to remain.

We now summarise the model assumptions and variable parameters. We first stipulate that hydrogen concentrations in the steel at the outset of the bake-out are initially determined by there being a uniform hydrogen activity throughout the steel, $(a)^2$. This will equal a fraction of a bar, as significant out-gassing of hydrogen will have occurred as it slowly equilibrates with the hydrogen activity of the surroundings – effectively zero in air - during an interim period between the time of removal of the equipment from service and the time of the bakeout. Due to the presence of traps, particularly in hydrogen damaged and poor quality steel, the last vestige of hydrogen will not escape from the

steel over a time frame of weeks or even years. An initial model hydrogen activity should not therefore exceed, say, 0.1 bar, but should not be lower than, say, 10^{-8} bar.

From this uniform activity through steel, we can calculate the trapped and free (diffusible, or lattice) hydrogen present at any depth of steel, having attributed within our model characteristic trap densities, enthalpies and uniform entropy at ‘background’ and at ‘hotspot’ depths¹⁰. We also require a density of lattice sites for hydrogen diffusion, which is usually invariant for mild steel. An example of variable parameters is shown in the **Table 1**, for the intensely measured site H, together with units adopted.

With regard to temperature, real initial, final and ramp temperatures and times were used, which very closely approximate to actual recorded values from the steel surface thermocouples. The rate of temperature equilibration through the steel is slow as compared with both the fastest rate of hydrogen diffusion, and the rate of temperature increase, and that therefore the temperature through the steel can always be assumed to be at a steady state. By making measurements of temperature at the stabilised bake-out temperature, we confirmed that the temperature of the dome interior face was consistently some 30 degrees less than at the entry face (280 vs 310 °C). We suppose this 10% temperature loss is uniform through the steel at all times.

The flux output from both the exterior and interior faces according to the values quoted in **Table 1** for site H is shown in **Figure 9**. Other peaks in **Figure 6** can be well modelled, again, by appealing to a ‘hotspot’ of an increased density of moderately deep traps within the 5 to 15 mm of the exterior face of the baked out dome. This is exactly where TOFD revealed laminations in nearby cut-away steel. The model therefore supports our conclusion above, that prior to detectable lamination, substantial hydrogen uptake can occur within a specific steel zone.

Further, exploratory use of the model revealed the effect of the temperature gradient (10% from one side of the steel to the other) was to generate a flux about 20% lower from the non-heated face, during one-sided charging, for a given distribution of trap densities, as compared with uniform heating. The results presented in **Figure 9** therefore approximately represent the situation prevailing if high hydrogen trap densities, laminations and blistering occurred about one fifth from the *entry* (interior) face of hydrogen, as can frequently be the case. In many bakeout scenarios one only has access to exterior sites, which would indicate the flux obtained in this work at interior sites, A’ to H’, **Figure 6**, if the trap density distribution were inverted at the steel centerline. Since this work demonstrates that substantial hydrogen trapping at any particular depth cannot be assumed from prior indications of laminations, a conservative estimation of ‘safe’ hydrogen efflux during bakeout is therefore quite low.

Most sites show a slight dip in hydrogen concentration at 16:00 hr, which is difficult to attribute to the model. One of the model’s limitations is the invocation of uniform diffuse flat traps in any plane parallel to a efflux surfaces. The diffusion coefficient – even at 300 °C – pertaining to any plane of deep and dense hydrogen traps will be unavoidably so low as to prevent hydrogen from substantially traversing it. A model in which hydrogen

'hotspots' were more segregated would allow for waves of hydrogen to progressively efflux from steel from hotspots at progressively increasing depths from a monitored surface. It would also be more realistic.

CONCLUSIONS

The monitored pre-weld bakeout on the perimeter of a 5 cm thick steel cut-away, ex-HFA service, near indications of lamination and blistering supported the need for the bake-out. Indeed, at the time, a prolonged bake-out was instigated on the basis of monitored flux; a decision which was fully justified given the more comprehensive analysis provided in this work. More hydrogen was collected from sites more proximal to the positions of blisters and laminations in steel that had been cut away, and where lamination growth had been most active prior to removal from service, even though there was no indication of hydrogen damage at these sites. Further, modelled flux profiles using authoritative literature values for ambient hydrogen activity in the steel, trap densities and energies, and data from the field pertaining to the steel geometry, bakeout temperature excursion, temperature distribution through the steel, provided good agreement with recorded data upon hydrogen trap 'hot spots' at a depth of some 10 mm from the bakeout surface, corresponding to the depth of nearby, detectable hydrogen damage.

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TABLES

Table 1. One-sided bakeout model. Notes: 1, parameters estimated or defined by the actual bake-out; 2, values derived from literature values, notably Grabke and Riecke¹², who developed the flat trap model of McNabb and Foster¹³, on which the bakeout model was based; 3, values optimised within sensible limits to obtain close fit with real efflux profile of site H, reproduced in **Figure 9**.

<i>Parameter</i>	<i>value</i>	<i>units</i>	<i>Description</i>	<i>notes</i>
w	5	cm	Steel thickness	1
P _{exp}	3586	[see eq. (ii)]	Steel permeation exponential coefficient	2
P _{pr-exp}	0.000335	[see eq. (ii)]	Steel permeation pre-exponential coefficient	2
d(hotspot)	1.05	cm	Hotspot average depth from heated surface	2
w(hotspot)	0.04	cm	Hotspot thickness	3
T ambient	298	K	Ambient temperature	1
T max	583	K	Maximum temperature	1
T loss	10	%	T loss through steel to ambient	1
T ramp	0.0382	K/s	Bakeout ramp rate	1
Activity	0.00002	Bar ^{1/2}	Initial H activity throughout the steel	3: see text discussion
N(ft,bgd)	0.0005	mol/cm ³	Background flattrap site density	1
N(ft,hot)	0.08	mol/cm ³	Hotspot flattrap site density	1
N(lattice)	0.253	mol/cm ³	Diffusible H site density	2
ΔH(bgd)	-23900	J/mol	Background flattrap enthalpy	2
ΔH(hotspot)	-36800	J/mol	Hotspot flat-trap enthalpy	3
ΔS	-10	J/mol.K	Flat trap entropy	2

FIGURES

Figure 1. Photograph showing top of dome, lamination and blister zones, and boundary of cut-away section. The ellipse shows the approximate cut-away perimeter. Some bakeout probe locations are indicated with letters. The arrow indicates the direction of lamination growth prior to removal from active service, also shown in **Figures 2b** and **8**.

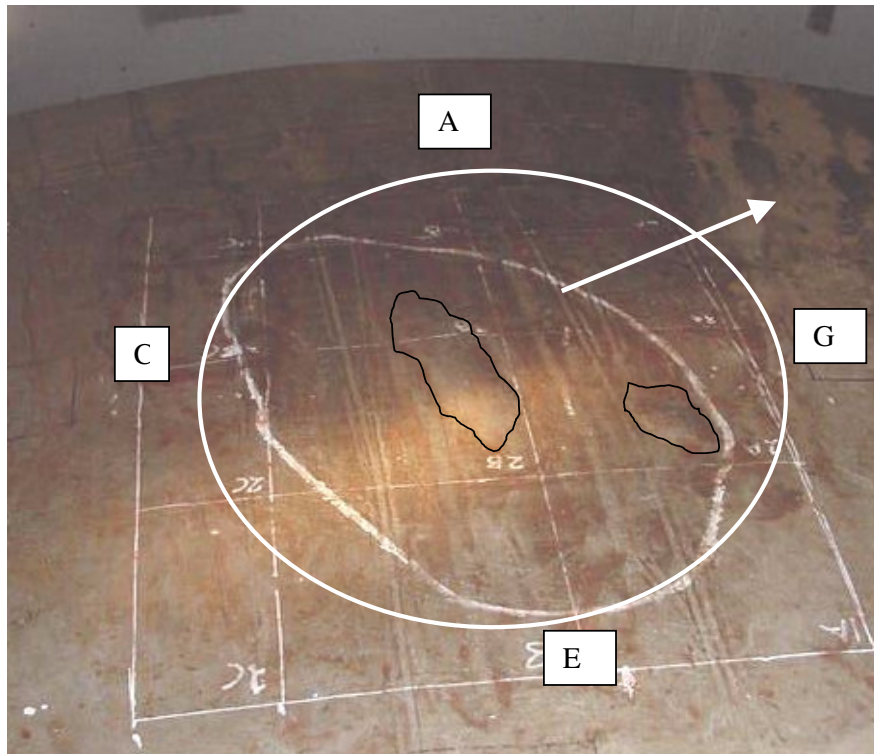
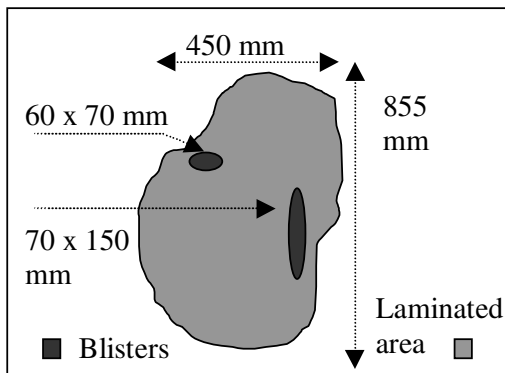


Figure 2. Blister and lamination growth as determined by USTM at 0° between **a**, Sept, 1999 and **b**, Dec 2000. The arrow indicates the direction of lamination growth prior to removal from active service.

a



b

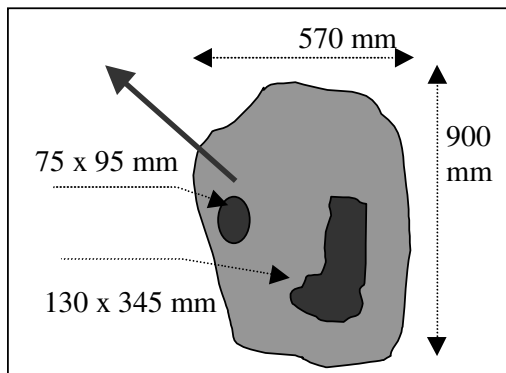


Figure 3. a, photograph taken shortly before installation of probes between alternate heat-pads as indicated for two probe sites D and E. **b**, complete heat treatment apparatus showing position of probes. The probe A capillary is connected to just visible gas sample conduit leading out of the picture to the hydrogen flux analyser.

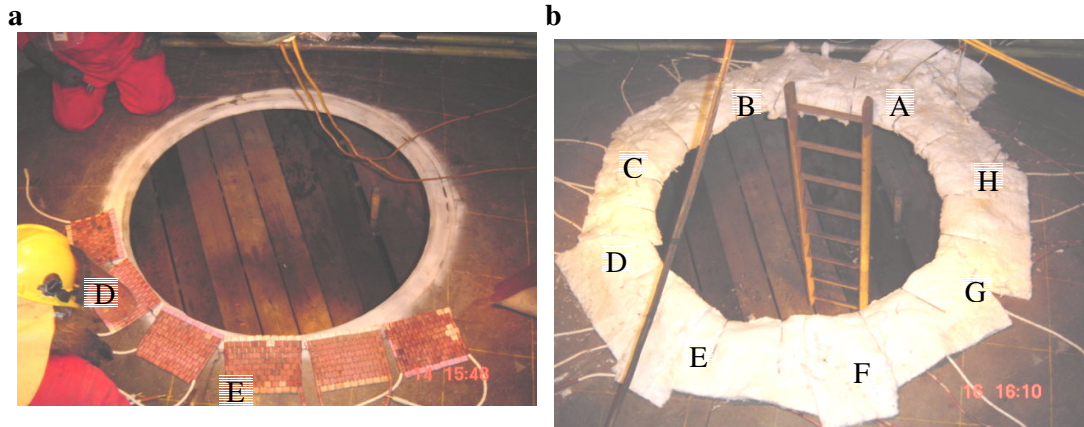


Figure 4, a low temperature roaming probe **b**, high temperature probe plate, incorporated under heat-pads during bake out. **c**, high temperature roaming probe.

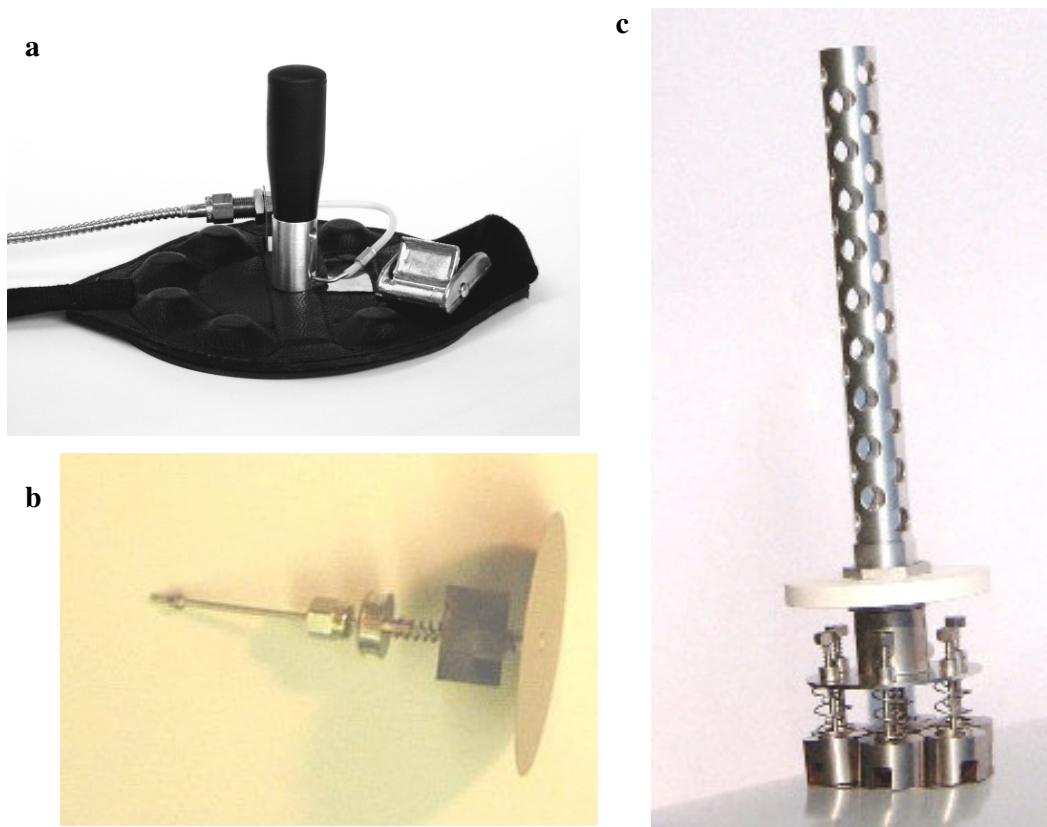


Figure 5. Schematic showing hydrogen temperature collector location under heat-pads in cross section.

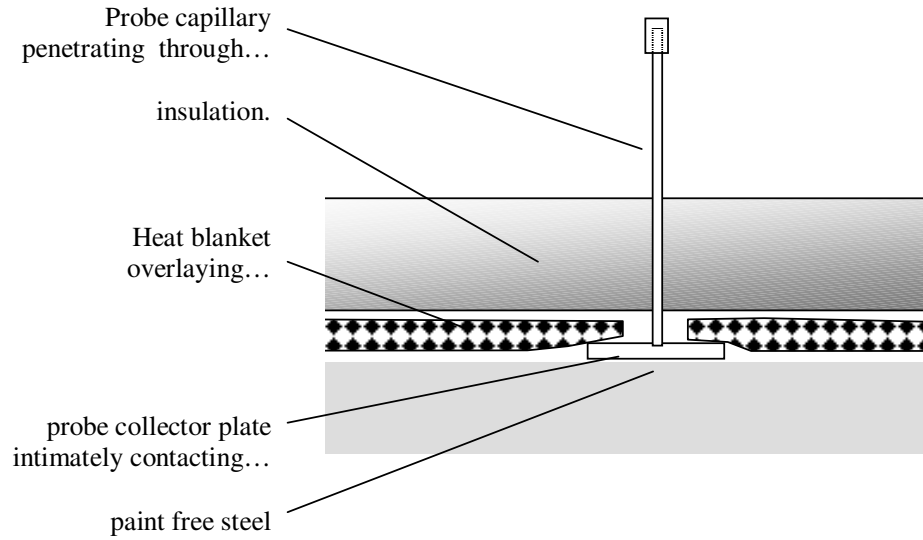


Figure 6. All flux measurements carried out in the field, during the period of bake-out, at sites identified in **Figure 4b**, together with the exterior, heated surface cycle temperature (continuous line). Symbols annotated 'Mon.' correspond to continuously monitored, as opposed to spot measurement data.

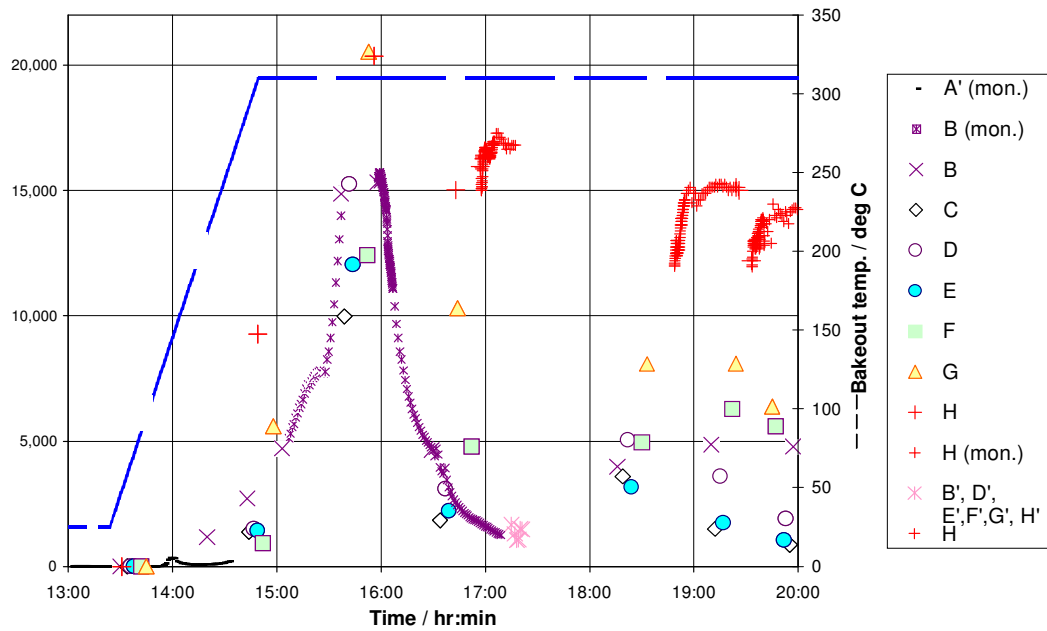


Figure 7. Flux measurements carried out in a column bakeout . The steel was of identical thickness, subject the same temperature cycling regime as the acid storage vessel dome bake-out featured in this work. The flux measurement approaches the detection limit of the HT collector used on sites A and B. The larger LT collector was used at site C; note the finer resolution. Gaps in data occurred at times of using probes to survey nearby equipment, where, as below, flux was less than 1% of typical flux values obtained from the vessel dome bake-out.

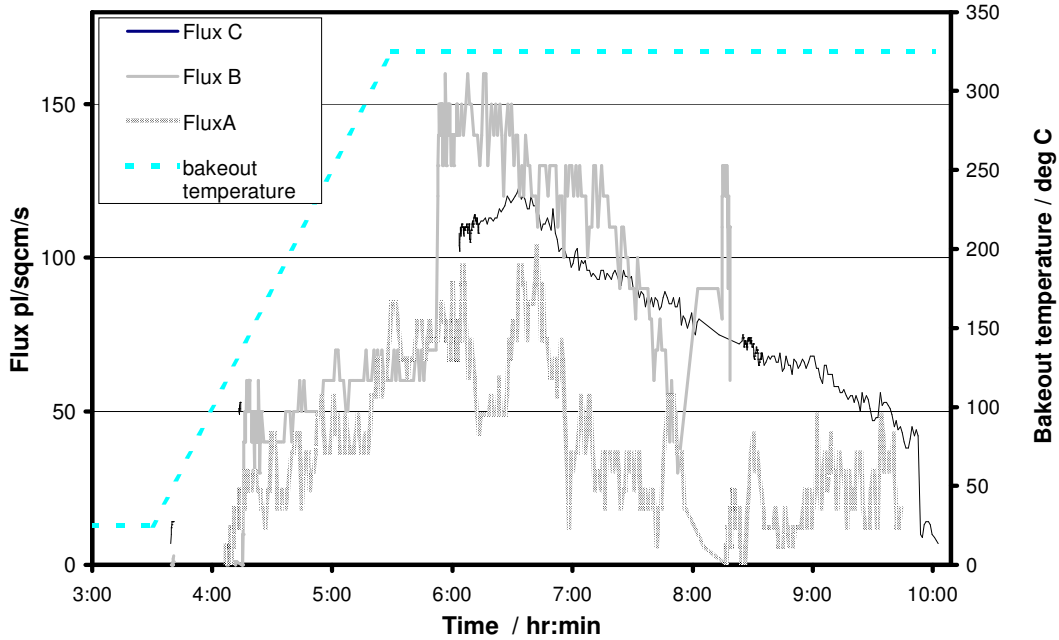


Figure 8 illustrating the relative total volumes of hydrogen emanating from the steel at the monitored test sites on the dome exterior surface during the initial bake-out, expressed as ppm (H in steel by wt) x depth (cm). Site H delivered 0.40 ppm.cm. The arrow indicates the direction of lamination growth prior to removal from active service.

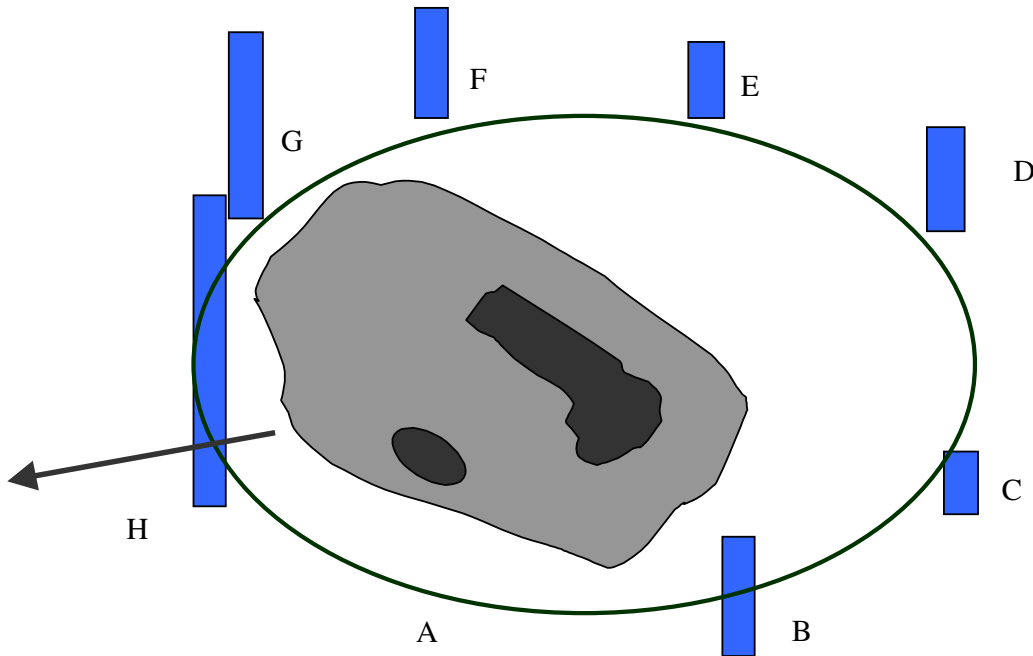


Figure 9. Model of site H data using values quoted in **Table 1.**

