

# **A LABORATORY STUDY OF TYPES OF CORROSION INDUCING HYDROGEN PERMEATION THROUGH STEEL**

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## **ABSTRACT**

This work investigates aqueous corrosion scenarios of industrial interest which induce hydrogen permeation through steel at 20-25 °C, and which are therefore amenable to hydrogen flux monitoring of steel corrosion at ambient temperatures. Initially, it was established that hydrogen flux exiting steel as a result of corrosion induced steady state hydrogen entry at the opposing surface was increased some by removal of air-formed thick oxide films, mitigated by the in-filling of hydrogen traps produced thereby. This informed the development of a procedure for sequentially exposing one face to corrosion for 10 minutes, followed by rapid subsequent measurement of efflux from that same surface. By means of this procedure we were able to rapidly ascertain that highly concentrated H<sub>2</sub>SO<sub>4</sub> and HClO<sub>4</sub> induce substantial hydrogen entry into steel. 48 wt% HF acid initially induces hydrogen flux of some 20% flux generated by sour gas saturated NACE A solution.

Key Words: flux, permeation, HFA

## **INTRODUCTION**

Use of non-intrusive hydrogen flux monitors on the external surface of mild steel pipes and vessels to indicate internal corrosion activity can be significantly less costly and complicated than the installation of intrusive devices. Non-intrusive flux probes provide a more inferential measurement of corrosion than intrusive probes, particularly from steel of more than 2 cm thick and less than 50 °C, through which the hydrogen transience time is typically more than a day. However, non-intrusive flux monitors minimally affect the corrosive environment itself. They also enable rapid mapping of prospective types of corrosion over wide areas.

Furthermore, non-intrusive flux probes can be extremely sensitive. The lower detection threshold of equipment used in this work is 1.4 pL/cm<sup>2</sup>/s (pL hydrogen gas at 20 °C and 1 bar per cm<sup>2</sup> steel surface)<sup>1</sup>, generated by a current density due to the sequential reaction



of 11 nA/cm<sup>2</sup>, for which the corresponding 11 nA/cm<sup>2</sup> anodic current due to Fe(solid) → Fe<sup>2+</sup> (solution) will dissolve 0.0001 mm steel per year<sup>(1)</sup>! In most circumstances a substantial proportion of cathodically generated hydrogen does not permeate the steel according to (2), instead, forming molecular hydrogen which desorbs at the entry surface:



In this work we present a very simple laboratory technique for the rapid investigation of aqueous corrosive scenarios giving rise to significant hydrogen entry in steel by the summary reaction (1). The objective was not to further characterise well known occluders in aqueous solutions, being the hydrides of S, Se, Te, P, As and F, as set out in the work of, for example, Newman and Shrier<sup>2</sup>. Rather, it was to address the role of the steel surface itself, and other constituents in corrosive liquors which might enhance, suppress, or have no affect on hydrogen occlusion.

The technique required flat steel test surfaces of >6 cm diameter and >3 mm depth in the following sequence:

1. Preparation
2. Exposure to corrosive liquor
3. Removal from liquor
4. Efflux measurement.

Our approach was first to investigate how steel surface preparation might affect the *exit* of hydrogen from steel, *viz*, reaction (3), by efflux measurements on steel plate through which a steady state flux was established. By this means, in step 1 we would assure a surface which would deliver reproducible efflux measurement, step 4. The effect of chemical treatment during efflux was also evaluated, to assess how chemical exposure during steps 2 and 3 might effect efflux during step 4. Finally we carried out the procedure on a range of both exotic and industrially significant chemicals purported to induce hydrogen entry into steel.

## PROCEDURE

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<sup>(1)</sup> 1.40 pL(H<sub>2</sub>)/cm<sup>2</sup>/s = 1.14x10<sup>-13</sup> mol (H)/cm<sup>2</sup>/s = 11 nA/cm<sup>2</sup> (for H → H<sup>+</sup> + e<sup>-</sup>). For Fe(solid) → Fe<sup>2+</sup>, 11 nA/cm<sup>2</sup> dissolves 5.7x10<sup>-14</sup> mol(Fe)/cm<sup>2</sup>/s = 3.4x10<sup>-12</sup> g/s = 1.1x10<sup>-4</sup> g/cm<sup>2</sup>/yr = 10<sup>-4</sup> mm/yr.

Two steels were investigated, quench and tempered flat steel plate of 3 mm thickness, and a tempered 3.1 mm flat section of very low carbon steel, of compositions shown in **Table 1**.

Prior to every experiment all apparatus was thoroughly washed with deionised water of conductivity  $< 10^{-12}$  ohm.cm, to ensure all contaminants were removed. 99.99% nitrogen was used<sup>(1)</sup> for de-aeration of liquids and gas enclosures. All experiments were carried at an ambient temperature of 20-25 °C.

To generate sour gas (H<sub>2</sub>S), 10 g FeS powder was added to 60 ml 1M H<sub>2</sub>SO<sub>4</sub> in a 120 ml glass bottle containing a nitrile bung into which was inserted PTFE tubing, connecting the sour gas generator to a 50 ml gas bubbler. The FeS-H<sub>2</sub>SO<sub>4</sub> mixture was left for at least 30 minutes to ensure displacement of ambient air from the system, before admission to corrosive liquors. During experiments engaging H<sub>2</sub>S, the gas bubbler was visually monitored, and 5g of FeS added, or 10 ml 5M H<sub>2</sub>SO<sub>4</sub> added sequentially to ensure vigorous H<sub>2</sub>S flow.

Table 2 summarises the corrosive solutions used in this work. Chemicals were of analytical grade<sup>(2)</sup>, of purities indicated in the Table. pH were measured using a pH electrode<sup>(3)</sup>, except in the case of HF solutions, for which standard literature values of pH are presented.

Hydrogen flux measurements were carried out using a hydrogen collection probe<sup>3-5, (4)</sup>, discussed in more detail elsewhere<sup>1,6-9</sup>. In brief, this comprised a circular ‘collector plate’, attached to the test steel surface by magnets, whose underside included a spiral pattern of raised grooves. On attachment to steel by means of magnets, air was guided by means of the grooves between the collector and the test surface to a central capillary, and thence through gas conduit piping across a hydrogen sensor to a pump. The hydrogen flux  $J$  (pl/cm<sup>2</sup>/s) was calculated from the increase in hydrogen concentration registered by the detector,  $c$ , (ppm by volume), as calibrated by exposure to 100 ppm hydrogen in air, the flow of air  $F$  (cm<sup>3</sup>/s) as verified by a volumetric flowmeter<sup>(5)</sup>, and effluxing steel surface area  $A$ , according to the equation  $J = 1000F.c/A$ .

### ***Exit face evaluation***

To investigate the effect of steel surface preparation on hydrogen efflux, one surface of Plate Steel (Table 1) was ground with p120 SiC paper to remove oxide coating and any other surface contaminant. It was then bonded with epoxy resin to a polypropylene cylinder (110 mm x 64 mm inner diameter), to form suitable containment means for the corrosive solution, as shown in Figure 1a. Over this was placed a stainless steel lid with a rubber seal to form an air tight seal. Silicon grease was applied around the rubber rim and at pipe junctions to ensure effective exclusion of ambient air. The lid included

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<sup>(1)</sup> BOC-Edwards, UK

<sup>(2)</sup> Sigma-Aldrich, UK

<sup>(3)</sup> Hanna Instruments, pHep2

<sup>(4)</sup> Hydrosteel™ LT-R probe, Ion Science Ltd, UK

<sup>(5)</sup> Saga 3000, Ion Science, UK

two ports to enable the inward and outward flow of gases. Attached to the interior side of one port was PTFE tubing, terminating in a sparger at the steel base. The chamber was purged with nitrogen for at least 30 minutes prior to admission of pH 4.7 buffered NACE solution A. The corrosive solution was decanted from the air tight vessel directly into the cylindrical container, using PTFE piping attached to the outlet port of the container lid. A volume of 300 cc of corrosive solution was added. The flux probe was attached to the exit face of the steel plate, and demarcated around its perimeter to ensure repeatable positioning on detachment and reattachment.

Once a stable flux through the steel plate had been achieved with the outlined procedure, the probe was detached from the exit face and the exit face manually treated with SiC paper of specified grades or chemical agents liberally administered by means of saturated paper towels for 80 s. After treatment, the surface was wiped for a duration of 10 s with a dry towel to ensure all remaining residue was removed, before replacement of the probe. Demarcations on the exit surface ensured repeatable placement of the probe, and a stopwatch was used for all durations of the procedure. Software functionality allowed noting of events with the data received into the acquisition system.

### ***Entry-exit flux evaluation***

Apparatus was similar to that described above, as shown in Figure 1b. However, to ensure rapid transition between conditions of charge and discharge, the charging cylinder was in this case attached to the test steel by means of a rubber seal between them, which, prior to attachment, had been smeared with silicone grease. Also, the lid of the charging container comprised a copper disc (500 g) whose weight ensured that no leakage of corrosive solution would occur around the base of the container.

The procedure adopted was as follows:

1. The entry surface of the steel was prepared by grinding with P120 SiC paper until all surface coatings and defects were removed, then with P600 paper directed at right angles to the final direction of P120 paper such as to ensure complete elimination of 120 grooves. Within 10 s the cylindrical container and lid were placed on top of the ground steel, and nitrogen vigorously driven through it to ensure an anaerobic environment.
2. 25 ml corrosive liquor, pre-saturated with H<sub>2</sub>S, or purged with N<sub>2</sub>, was injected through the gas exit port by means of a 30 ml syringe. For H<sub>2</sub>S saturated solutions, the gas supply was switched to H<sub>2</sub>S. 600 ± 2 seconds were allowed to elapse, at which point a stopwatch was activated.
3. Within a target 10 s, and no more than 25 s, the lid was removed, and liquor content and containment walls manually swept from the steel plate into a separate waste receptacle. The steel was submerged in deionized water to remove any corrosive residue, towel dried, and placed on the bench for hydrogen flux measurement.
4. The hydrogen probe was then attached to the steel surface ensuring intimate contact with the face exposed to corrosive liquor in step 2. Surface demarcations on the collector

and target steel enabled rapid repeatable placement. Flux was recorded until it subsided to zero.

## RESULTS AND DISCUSSION

### *Exit flux evaluation*

In order to evaluate the effect of both surface treatment and chemicals on flux emanating from an exit steel surface, a steady state flux was generated through 3 mm plate steel identified in Table 1, by charging the opposing entry face with buffered NACE A solution, Table 3, solution 1. The initial flux transient is shown in Figure 2. The initial rise in efflux was slow as compared to what might be expected from diffusion limited control of hydrogen permeation through steel of 3 mm thickness, due to the time required for sour gas saturation of the 300 ml of NACE A buffered solution at the entry face. Smaller volumes of charging solution were found to cause entry flux conditions which were too variable on the time scale of exit flux variations induced by exit surface treatment encountered during pre-trials, namely, changes occurring over a few hours.

Once an invariant flux had been established the hydrogen collector probe was detached for 60 s and re-attached for 60 and 90 s as shown in Figure 2, points **a** and **b**, respectively. This exercise yielded a standard deviation in flux measurement delivered after 90 s probe attachment of 1% of the mean flux value obtained. The flux profile in subsequent days decayed approximately exponentially.

Over the period shown in Figure 3, the prevailing decay constant was 127 hr (*ie* decay by a factor of  $e \approx 2.7$  every 127 hr). During the time shown, two bouts of 85 s episodes of vigorous manual grinding of the efflux surface with P120 paper lead to a departure from this decay profile, anticipated in the absence of any such treatment, and shown as the smooth line in Figure 3. Note that during each bout of grinding, the criterion for a repeat grinding of the surface was that the flux had reached an approached a value stable to within 1.5 pL/cm<sup>2</sup>/s per minute.

After each episode of grinding, efflux *slowly* recovered to a new asymptotic value. **Figure 4** shows the flux response to one such episode, in contrast with the probe response to probe detachment and re-attachment. The hashed area curve corresponds to a volume  $V$  of hydrogen per unit area of steel ( $\mu\text{L}/\text{cm}^2$ ) which was not effluxed due to the preceding abrasion. Over all 15 grinding episodes  $V$  averaged  $3.86\mu\text{L}/\text{cm}^2$ , or approximately  $1.9 \times 10^{18}$  H atoms per  $\text{cm}^2$ . This should be contrasted with  $1.2 \times 10^{15}$  crystallographic sites for potential H chemisorption on alpha-iron. Allowing for a surface roughness factor of 2, the hydrogen 'deficit'  $V$  is some 75 times what would be expected from a simple requirement for pre-saturation of all available surface sites prior to the formation of hydrogen association at, and consequent desorption from steel, necessary for probe detection. Two effects may have contributed to the 'deficit'  $V$ :

A: Grinding will introduce a new, steel surface morphology, replete with empty hydrogen traps at the steel surface, requiring population by hydrogen prior to hydrogen efflux.

*B*: Freshly revealed steel may assist hydrogen oxidation by air, for example according to  $\text{Fe-H} + \text{O}_2 \rightarrow \text{Fe-O-O-H} \rightarrow$  iron (hydr-) oxides, decreasing hydrogen available for recombination and efflux until an oxide formed on the steel.

If *A* were pre-dominant, the deficit would be identifiable with a volume of hydrogen needed to fill traps introduced by grinding, achieved at a rate circumscribed by the sub-surface hydrogen flux; in contrast, effect *B* would be expected to affect efflux on a time dependent basis, defined by the rate of oxide formation, independent of flux. Since the average deficit for second bout of grinding was 96% of the first (3.78 vs 3.94  $\mu\text{l}/\text{cm}^2$ ), whereas the average end point flux of the second bout was 81% of the first, effect *A* was considered to pre-dominate.

For each bout of grinding, the most severe hydrogen ‘deficits’ as defined above, occurred subsequent to initial grinding episodes, as indicated by the 2000 s responses illustrated by open circles in Figure 3. This is again consistent with phenomenon *A* being the dominant cause of hydrogen deficit, as initial grinding would entail removal of a more air formed oxide, with consequently more disruption of the steel morphology. If phenomenon *B* was significant, initial hydrogen ‘deficits’ could only be expected to be *less* severe, due to incomplete oxide removal.

After each bout of grinding, a flux exceeding the decay profile for no surface treatment (broken line, Figure 3) was initially obtained. However, the actual profile then decayed until the anticipated profile was recovered. This is consistent with the formation of an oxide which substantially forms on a timescale of hours, the rate of formation decreasing with thickness. The flux from the air stabilized oxide film was some 90-95% of the maximum efflux obtained subsequent to mechanical oxide removal.

This interpretation of data presented was corroborated by our experience of abrasive removal of very aged coherent oxide films, such as formed on steel on excursions to high temperatures. This can lead to an increase in previously stable efflux (at ambient temperatures) of some 15-20%. We also noted that a partial recovery in flux over the initial minute time scale of probe response occurred when surface grinding was carried out over periods shorter than 90 s, or when finer grade SiC paper was deployed. In the context of the present work, trials such as presented in Figures 2-4 provided confidence that a steel surface, in air, ground with SiC paper, would deliver a steel surface whose hydrogen *exit* efflux characteristics were reasonably consistent, subsequent to trap filling. Further, by studies of the effect of chemical treatment of the exit surface on a pre-established steady state flux, an insight was gained as to the effect of oxides and surface morphology during hydrogen *entry*, the focus of this work.

Figure 5 shows the effect of 80 s wetting with sulfuric acid on a surface pre-ground with P120 paper 16 hr previously. Initial treatments (1.5 and 2.5 hr) caused temporary reduction in response, though hydrogen efflux deficits were only some 5% those caused by grinding. Progressively transient hydrogen peaks were observed, and steady state flux increased markedly. This behaviour is consistent with initial consumption of acid in the dissolution of iron oxide:



The prevailing hydrogen flux would be temporarily taken up in filling traps generated at the disrupted Fe-FeO interface. After two treatments, acid was available to react directly with steel, in the formation of hydrogen gas:



So it did, increasingly progressively, as shown from the surfeit hydrogen generated in the latter profiles illustrated in Figure 5. despite drying of the surface with toweling. Even 0.1 microliter of the 1M diprotic sulfuric acid per  $\text{cm}^2$  steel, as an evaporative residue, corresponds to 2,200,000 pl hydrogen gas. Moreover, the accumulative formation of  $\text{FeSO}_4$  on the surface by reactions (4) and (5) would continuously promote hygroscopic conditions for moisture abstraction from the air, and subsequent corrosively generated hydrogen formation.

Important conclusions could be drawn from this test. Every effort should be made to limit oxidation of uncharged steel prior to short-term (10 minute) exposure to prospectively hydrogen charging solutions, as these can and do require dissolution before any hydrogen generation at the steel surface occurs. Further, hydrogen probes dependent on the formation of molecular hydrogen at the sensed surface should not be used on substantially 'salty' surfaces, where condensation may promote acid hydrogen liberating conditions.

The exit face of Plate Steel subject stable sour solution induced efflux was exposed to nitrogen purged ammonium hydroxide, NACE A solution and deionised water, within a few hours of P120 paper grinding. The effect of water and NACE A solution, a typical example of which is shown in Figure 6, was a temporary  $\pm 10\%$  disruption to the flux. Ammonia yielded similar profiles. On no occasion did exposure to these neutral or alkaline solutions lead to hydrogen flux deficits, as consistently occurred subsequent to manual abrasion.

### ***Entry-exit flux evaluations***

The largest efflux recorded in consequence to 600 seconds exposure of a steel face to corrosive solutions, according to the four step procedure detailed above (see *Procedure*), was obtained from  $\text{H}_2\text{S}$  saturated NACE A solution. This is shown in Figure 7, together with the profile obtained from nitrogen purged NACE A solution. For an idealised steel, containing no hydrogen traps, the diffusion coefficient for the steel would be completely independent of hydrogen concentration. Consequently, one would expect flux values from any two solutions to be in strict proportion at all times elapsed since the steel was removed from a charging solution. This was not observed; weakly hydrogen charging solutions, such as obtained from the nitrogen purged NACE A solution, decayed from their peak flux values more rapidly than strongly hydrogen charging solutions. Both traps created during the pre-charge surface grinding, and pre-existing traps within the bulk metal explain this behaviour.

To compare the hydrogen occlusivity, that is, the hydrogen charging potential, of different solutions, the volume of effluxed hydrogen,  $V/cm^2$ , was calculated from the efflux profiles. Results for all solutions tested are shown in **Figure 8**.

#### *Cyanidic ammonia*

Saturation of ammonia solution with  $H_2S$  was expected to generate  $(NH_4)_2S$ , ammonium sulfide, which is known to lead to hydrogen induced cracking, especially in the presence of cyanide and must therefore occlude hydrogen. However, no hydrogen efflux was observed by such solutions, with or without the addition of potassium cyanide. It is suspected that hydrogen charging is induced by an *excess* of hydrogen sulfide, and that in the solutions tested, the formation of ammonium sulfide was incomplete.

#### *Strong acids*

Strong perchloric and sulfuric acid promoted substantial hydrogen entry. In the absence of a hydrogen occluder, it appears that the formation of high concentrations of chemisorbed hydrogen by reaction (1) on the low carbon steel surface was sufficient to induce substantial hydrogen entry. Hydrogen charging was low in the higher pH solution, 1M HCl.

#### *Hydrofluoric acid*

As a weak acid, hydrofluoric acid was identified as a hydrogen occluder, although the hydrogen volume effluxed from 0.2% hydrofluoric acid was negligible. Addition of 5% NaCl to 2.9% HF led to a lower hydrogen efflux. Since the NaCl would increase the conductivity of the solution, and hence enhance the rate of a corrosive reaction, it is suspected that the reaction of HF on steel does not proceed *via* an electrochemical mechanism.

## CONCLUSIONS

A procedure was developed by which solutions subject to hydrogen occlusion at 20-25 °C could be rapidly identified, without recourse to thin steel membranes. In development of this technique we investigated the effect of manual abrasion and treatment of chemicals on the hydrogen efflux promoted at a steel 'exit' surface by sour corrosion at the opposing 'entry' surface. Manual abrasion was found to cause a decline and subsequent recovery in flux consistent with the formation of hydrogen traps by grinding, and, over a timescale of a few hours, their in-filling by permeating hydrogen, and the re-establishment of a stable oxide film in air. Chemical treatment led to a modest disruption in pre-stabilised efflux, probably due to changes in the exit surface morphology. The entry-exit procedure developed confirmed the hydrogen occlusivity of sour and HF solutions.



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## TABLES

**Table 1.** Compositions of steels used in this work, as determined by Atomic Emission Spectrometry<sup>(1)</sup>.

	C	Si	Mn	P	S	Cr	Mo	Ni	Al	Co	Cu	Nb	Ti	V	B	N	Fe
Plate	.19	.01	.9	.013	.005	.02	.00	.01	.317	.00	.00	.00	.000	.00	.00	.085	98.73
Low C	.025	.01	.03	.009	.013	.0	.00	.02	.039	.00	.00	.00	.000	.00	.002	.031	99.86

**Table 2.** Corrosive solutions used in this work. The balance of these solutions was deionised water. Except as noted, all solutions were initially purged with nitrogen. ‘\*’ designates a solution that was, on occasions, subsequently saturated with H<sub>2</sub>S, as identified in the text.

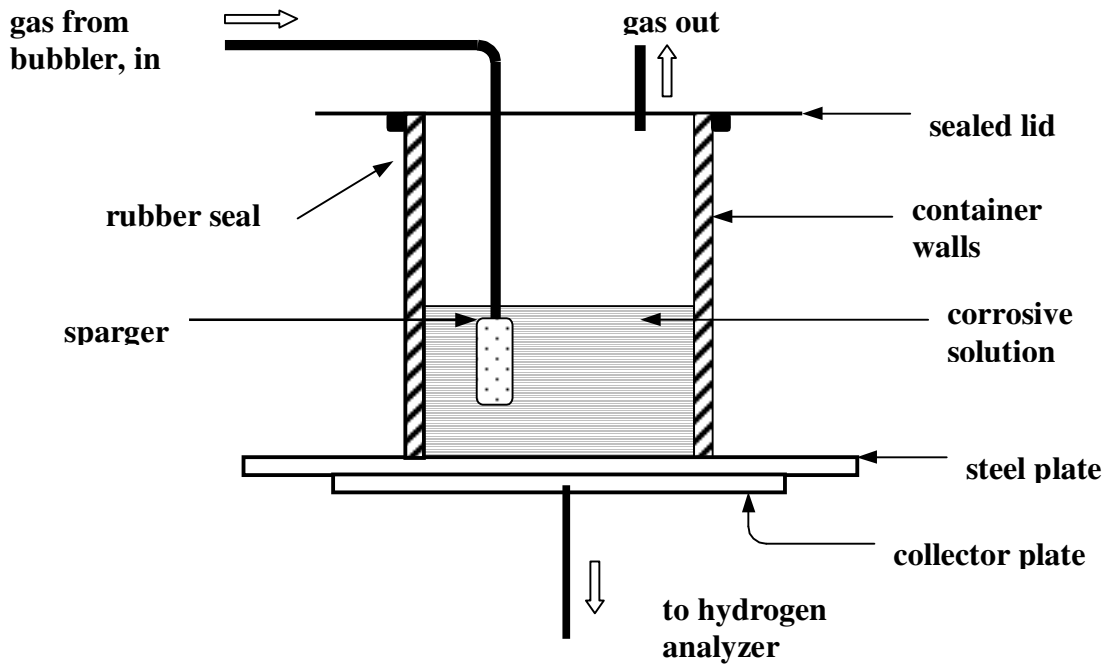
No.	Description	Composition	pH	Remarks
1	NACE A	5% NaCl (99.9%), 0.5% acetic acid (>99.7%), 0.75% sodium acetate (>99%)	4.7 to 4.9	*buffered NACE A solution
2	1 M HCl	3.8% HCl (>99.99%, as 37% in water)	0.1	
4	1 M sulfuric acid	10.2% (>99.99%)	0.3	
5	1.5 M perchloric acid	15.4% HClO <sub>4</sub> (>99.99%, as 60% in water)	0	
6	Lemon juice	Reconstituted from concentrate	3.0	* lemon juice <sup>(2)</sup>
7	Cyanidic ammonia	21.9% NH <sub>4</sub> OH, 0.1% NaCl, 1.25% KCN	9.0	* Cyanide added after H <sub>2</sub> S saturation
8	X% HF	X% HF (48% in deionised water)	Var.	Access of air to HF restricted. Balance N <sub>2</sub> purged deionised water
9	HF/NaCl	2.9% HF and 5% NaCl		As above.
11	Ammonium hydroxide	29% (<0.002% ign. residue, as 29% in water)	12.4	

<sup>(1)</sup> Spectrolab M7, Spectro, Germany

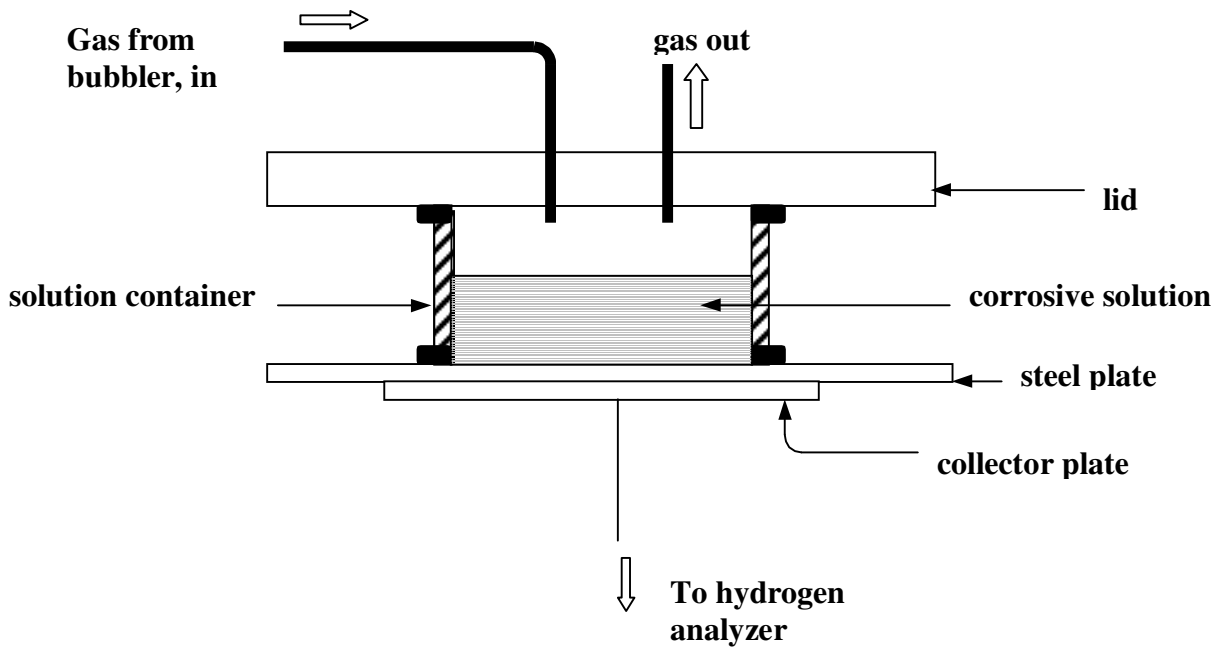
<sup>(2)</sup> Jif™

## FIGURES

**Figure 1a.** Schematic representation of equipment used in exit surface flux evaluation



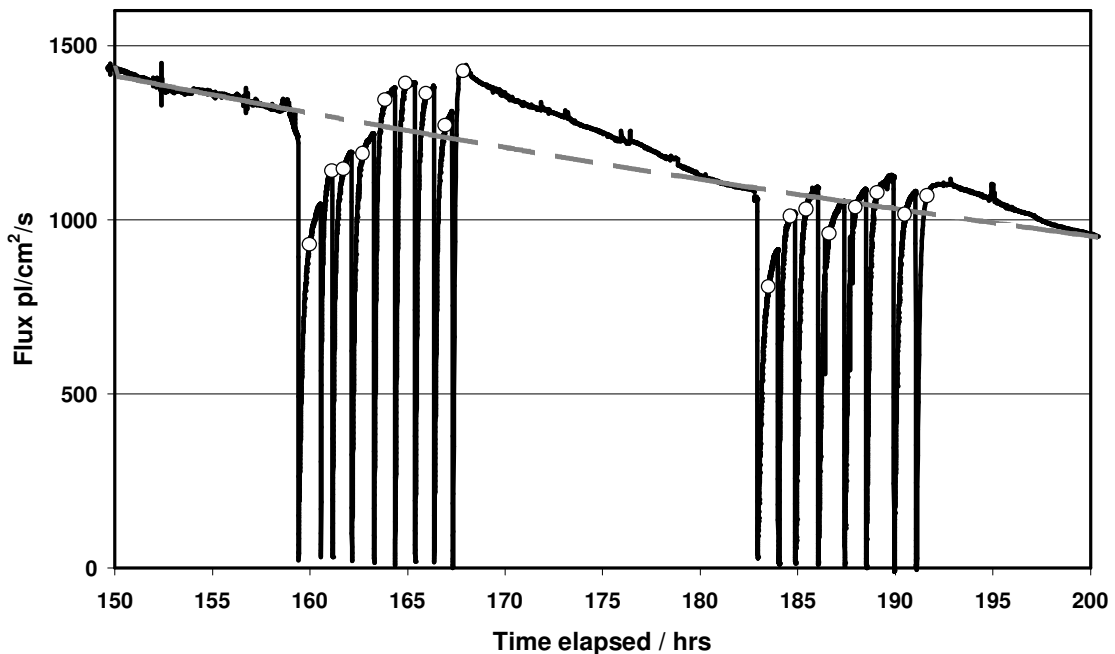
**Figure 1b.** Schematic representation of equipment used in entry surface flux evaluation



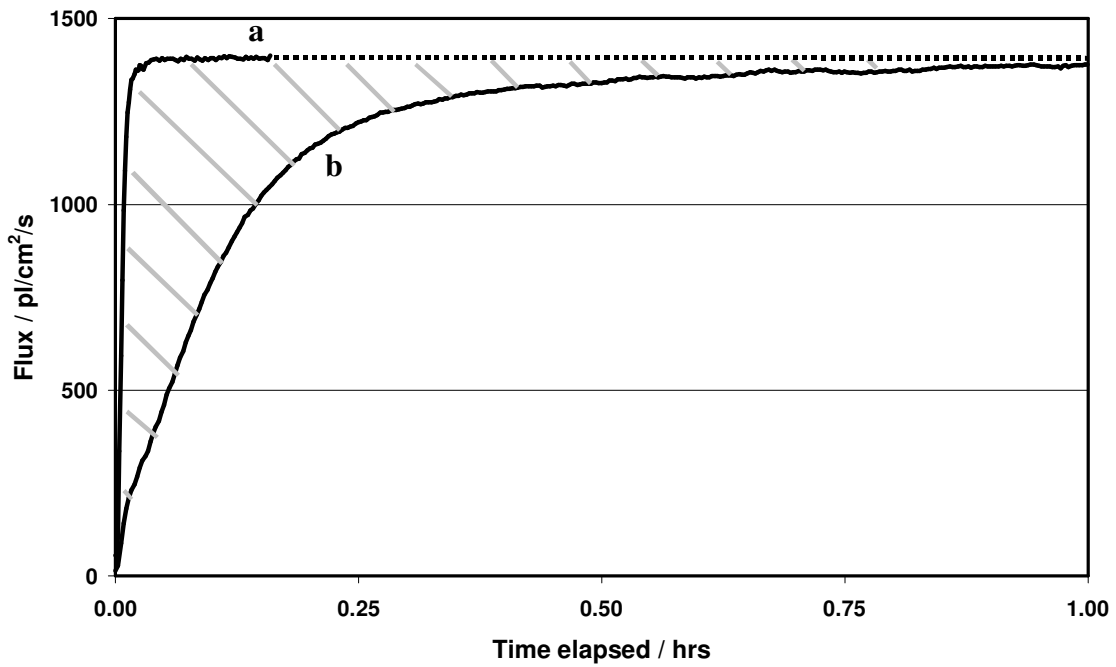
**Figure 2.** Hydrogen efflux onset at exit face of 3 mm Plate Steel following commencement of H<sub>2</sub>S saturation of NACE A solution at opposing entry face. Effect of probe detachment, 60 s, and re-attachment for **a**, 60 s seconds and **b** 90 s.



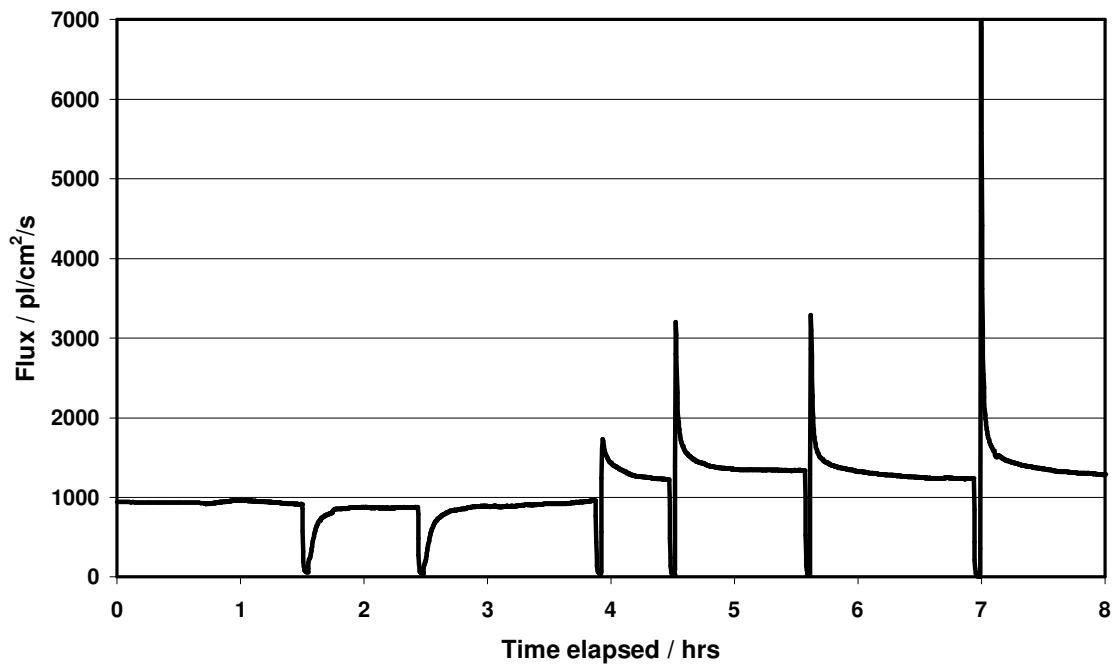
**Figure 3.** Effect of probe detachment, 80 s manual abrasion of steel exit surface with P120 SiC paper, followed by probe re-attachment on prevailing efflux transient obtained about a week after commencement of the experiment shown in **Figure 1**. Flux readings 2000 s subsequent to probe re-attachment are shown by open circles. The anticipated exponential decay profile for efflux without pre-treatment is shown as a broken line.



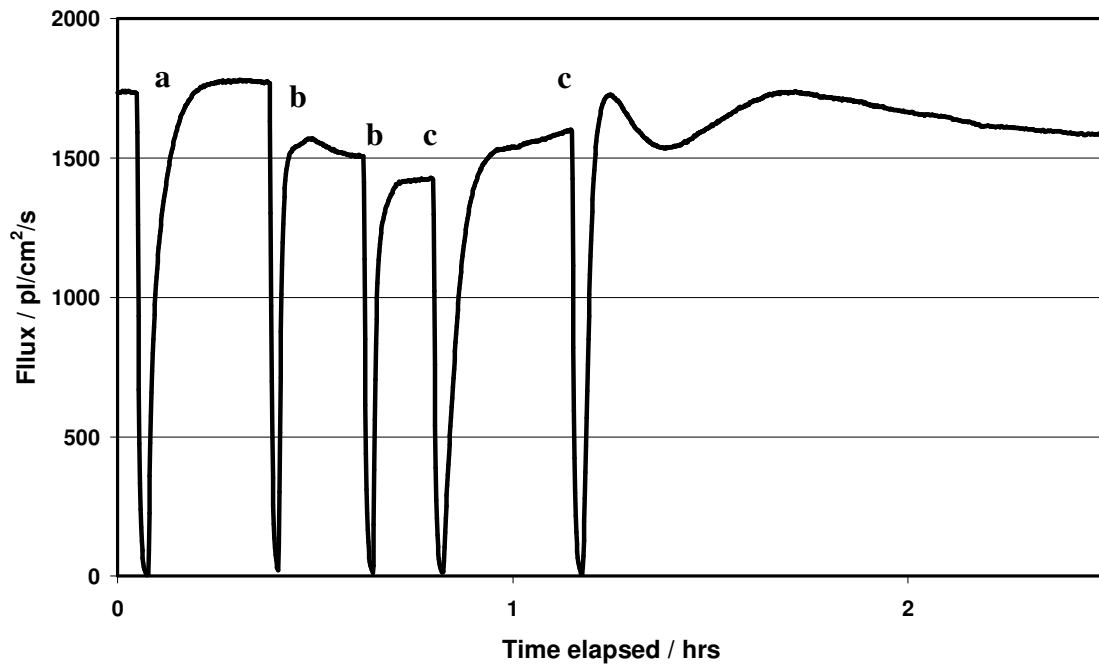
**Figure 4.** Detail illustrating 'hydrogen deficit', the area encompassed between this profile and a flux profile obtained in the absence of grinding. **a**, from **Figure 2** (2.6 hr); **b**, from **Figure 3** (164 hr)



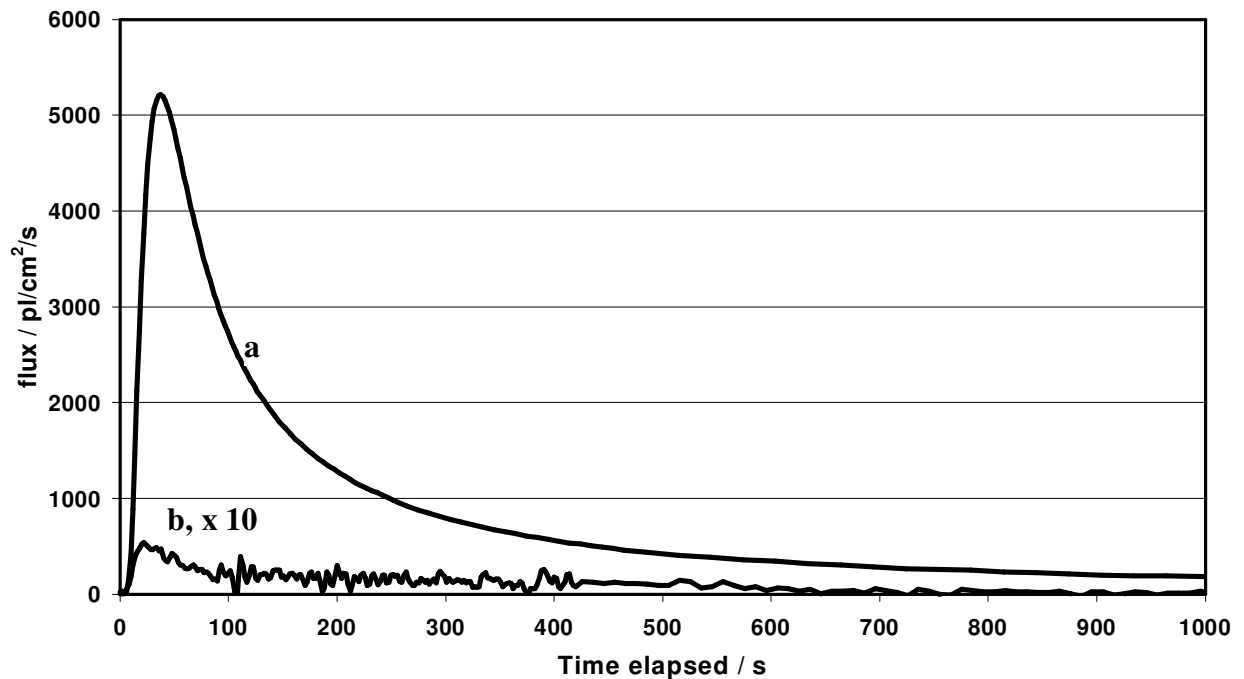
**Figure 5.** Effect of a series of 85 s treatments of an effluxing steel surface with 1 M sulphuric acid, applied manually with towelling soaked with the acid.



**Figure 6.** Effect of sequential treatments of an effluxing steel surface for 80 s. **a**, manual grinding with P120 paper; **b**, de-ionised water, and **c**, nitrogen purged NACE A solution.



**Figure 7.** Efflux from a low carbon steel surface obtained within 10 s of 600 s exposure to **a**, H<sub>2</sub>S saturated NACE A solution, and **b**, nitrogen purged NACE A solution, flux scale x 10, for clarity.



**Figure 8.** Total volume of hydrogen until the flux subsided to zero ( $\mu\text{l}/\text{cm}^2$ ) collected from a low carbon steel surface following 600 s exposure to various solutions. '+ H<sub>2</sub>S' indicates sour saturation prior to and during the solution exposure. Otherwise the solution was nitrogen purged throughout. For solution details see **Table 2**. L.J., lemon juice.

