

### A REVIEW OF HYDROGEN FLUX PROMOTERS

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#### ABSTRACT

This paper provides a concise review of 'hydrogen promoters', aqueous corrodants known to generate hydrogen flux through mild steel at low temperatures. A new theory of hydrogen promotion will be presented. Hydrogen promoters will be ranked according to their severity. The role of temperature, scale, surface coatings and surface condition will also be considered.

The paper should provide useful reference material for those interested in field and laboratory measurements of hydrogen flux, and the relation between the two.

Keywords: hydrogen flux, hydrogen flux promoter, sour corrosion

#### INTRODUCTION

Certain non-metal hydrides are known to be strong hydrogen promoters <sup>1-5</sup>. These cause enhanced entry of hydrogen into corroding metal, in particular carbon steel, and subsequent hydrogen flux through the metal which is orders of magnitude higher than the flux generated by a comparably corrosive, non-hydrogen promoting corrodants under the same conditions.

Hydrogen is formed on metals, as a result of impressed or corrosive cathodic reduction of aqueous protons:

$$\mathrm{H}^{+}_{\mathrm{aq}} + \mathrm{e} = \mathrm{H}_{\mathrm{ads}}$$

The subscript 'ads' indicates adsorption on the metal surface. In non-promoting acids the hydrogen so formed predominantly recombines or associates:

$$H_{ads} + H_{ads} = H_{2 ads}$$

and then bubbles off. A promoter causes a much larger proportion of hydrogen to enter the metal, most notably carbon steel, rather than recombining according to reaction (ii).

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(i)

(ii)

In 1969 Newman and Shreir<sup>5</sup> presented authoritative data on the relative strength of certain strong hydrogen promoters identified by Smialowski *et al.*<sup>4</sup> and found them to be active as the hydrides  $H_2S$ ,  $H_2Se$ ,  $H_2Te$ ,  $PH_3$  and AsH<sub>3</sub>, a conclusion supported by Bockris<sup>2</sup>.

The chief industrial interest in promoters then, as now, was the risk of hydrogen embrittlement and damage caused to steel by hydrogen entering steel at very high activities due to the very powerful promoter hydrogen sulfide. Of course, much has since been done to develop corrosion inhibitors which prevent sour corrosion, and to manufacture steels and welds which are not susceptible to sour corrosion induced hydrogen damage. However, as oil is produced from older and deeper reservoirs, so, it appears, the sulfur content of produced crude has increased, leading to more severe sour corrosive service environments that have to be faced in oil production facilities and refineries. In the case of refineries, the effect is more severe as equipment was not necessarily designed to cope with severe sour corrosion.

In recent years there has come to light much more data on promoter action, including data for hydrogen fluoride, which provides a vital clue as to the mechanism of hydrogen promotion. By considering old and contemporary data, a mechanism for promoter action can be developed, which fits the facts much better than the conventional theory of promoters acting to 'poison the hydrogen association reaction' (ii). Moreover, with contemporary measurements of hydrogen flux, it is possible to now offer a universal index of promoter strength.

#### THE MECHANISM OF HYDROGEN PROMOTION

Recent studies agree as to the very weak dependency of hydrogen entry on the concentration of a promoter <sup>6-9</sup>, several authors concluding that steady state hydrogen flux,  $J_{\infty}$  varies as  $[H_2S]^{1/4}$  <sup>6-8</sup>. It therefore seems likely that the promoter acts catalytically at the metal surface to facilitate hydrogen entry.

The chemical elements associated with hydrogen promotion are identified in Figure 1. The broader chemistry of hydrogen with the chemical elements is also shown, to illustrate that promoters of hydrogen may effect a large swathe of hydrogen permeable metals.

The strong promoters have little in common. H<sub>2</sub>S, H<sub>2</sub>Se and H<sub>2</sub>Te and HF are all weak acidic, but PH<sub>3</sub> and AsH<sub>3</sub> are neither basic nor acidic. It is significant that there are many organic weak acids - and water - which are not strong hydrogen promoters. The promoters, apart from hydrogen fluoride, HF, have energetically accessible empty orbitals (*d*-orbitals) which could enable electrons to be accommodated in a low energy transition state facilitating hydrogen entry. This is a frequently encountered trait of catalysts. Moreover, the conjugate base of HF, the fluoride ion, complexes with HF to form [F-H-F]<sup>-</sup>. This surely indicates a unique feature of strong hydrogen promoters. *All strong hydrogen promoters can form stable adsorbates on a metal which include a bonded hydrogen atom.* 

Newman and Shreir<sup>5</sup> identify 'an almost linear' relationship between hydrogen – promoter element bond strength and promoter strength, which they explain as being due to the promoter weakening the Fe-H bond. However, this explanation must be incomplete, being valid for diatomic hydrides for which there is no evidence of hydrogen promotion in the literature. Their observation that the weak acid promoters  $H_2S$ ,  $H_2Se$  and  $H_2Te$  cause maximum hydrogen entry into mild steel at a pH (4.5, 3.0 and 2.2 respectively), at which they are appreciably at equilibrium with their conjugate bases (pH 6, 2.8 and 1.8 respectively) have not been confirmed by other work<sup>8,10-11</sup> and care must be taken, with sour gas at least, that, in the absence of cyanide, promoter corrosion product is insoluble and passivating at pH >3-5 depending on minor alloy constituents<sup>12</sup>.

It should be further noted that permeation flux varies as the square root of applied cathodic current <sup>4,13-14</sup>. This is thought to be due to the predominance of the second order reaction on steel by which hydrogen formed by reaction (i) ultimately bubbles off, reaction (ii). It is very likely that the view of surface adsorbed hydrogen atoms on steel predominantly recombining has led to the notion that promoters act as 'catalytic poisons', *ie* obstructing hydrogen surface migration and combination. Although this is perfectly feasible, it does not explain the observation that

promoting elements can bond with at least two hydrogen atoms, or that the promoter is required in only catalytic quantities.

A mechanism for hydrogen promotion, congruent with all the evidence, would suggest that the conjugate base of the hydrogen promoter absorbs (or is electrochemically formed) on the steel surface, and catalytically promotes hydrogen entry through a transition state complex  $[HSH]^*_{ads}$  resembling the promoter hydride. For example, for H<sub>2</sub>S,

$$H_{ads} + SH_{ads} = [HSH]^*_{ads} = HS_{ads} + H_{Fe}$$

shown pictorially in Figure 2. In reaction (iii), one hydrogen is shown in bold type to emphasise that the hydrogen attached to the promoter is replaced during hydrogen entry. In Figure 2 an equivalent reaction for HF is also presented.

(iii)

(iv)

(v)

Smialowski<sup>4</sup> and Newman and Shreir<sup>5</sup> propose that the promoting action of Group V elements P, As and Sb occur over the entire pH range, because these hydrides do not hydrolyse at high pH. However, hydrogen promotion by these elements has only been reported where these hydrides could form electrochemically. For example, in the case of arsine, hydrogen permeation occurs at potentials where dissolved  $As_2O_3$  or  $NaAsO_2$  are electrochemically reducible to  $As_2H_3$ . So it is entirely plausible that promoted H entry proceeds via a reaction analogous to (iii) in the case of arsine.

An alternative to reaction (iii) could be

$$H_{aq}^{+} + SH_{ads} + e = [HSH]_{ads} = HS_{ads} + H_{Fe}$$

though it is hard to reconcile this with the square-root dependency of flux on applied cathodic current.

#### A SCALE OF PROMOTER STRENGTH

Promoter strength has previously been assessed <sup>5</sup> from bulk hydrogen concentrations of mild steel coupons fully immersed in corrosive solutions containing various promoters. These concentrations do not provide for a widely applicable scale of promoter strength, because different mild steels – even from the same manufactured plate - have different solubilities for hydrogen, not least at the temperatures of aqueous corrosion, where a substantial proportion of hydrogen is dynamically distributed between traps and lattice diffusion sites. A more universal comparison of promoters would be provided by the hydrogen activity they generate. According to Sievert's Law, the concentration of hydrogen in steel, c (Ncm<sup>3</sup>.cm<sup>-3</sup>)<sup>(1)</sup> varies as square root of hydrogen gas pressure p (bar) with which it is in equilibrium. So if we define S (Ncm<sup>3</sup>.cm<sup>-3</sup>.bar<sup>-1/2</sup>) as the solubility of hydrogen at the prevailing temperature and at one bar, activity of hydrogen in steel we can define hydrogen activity a as

$$a = c / S = p^{1/2}$$

The promoted hydrogen activity in steel  $a_{Pr}$  generating a hydrogen concentration in steel *c* is then equated with a gaseous hydrogen pressure *p* (bar), *ie* an equivalent pressure of gaseous hydrogen which would be in equilibrium with the *c* at the same temperature. This is an extremely useful concept and provides a route to quantify promoter strength.

For sufficiently thick metal plate of thickness w (cm)<sup>8,9,15</sup>, subject to hydrogen entry on one side, hydrogen activities is surface reaction controlled, and correspondingly, removal of hydrogen into the steel is negligible. Then

<sup>&</sup>lt;sup>(1)</sup> Note 1 Ncm<sup>3</sup> .cm<sup>-3</sup> = 11.2 ppm hydrogen in steel by weight. Concentrations and solubilities within this document will be expressed in ppm, as is much more common. Ncm<sup>3</sup> refer to cm<sup>3</sup> of (hydrogen) gas at one bar and 0 °C. The point of using Ncm<sup>3</sup> is that it allows for unitary equivalence in equations (vii) and (viii).

the hydrogen activity at the corroding metal (hydrogen entry) sub-surface,  $a_0$  is determined by equation (v) and can be equated <sup>(2)</sup> with  $a_{\rm Pr}$ :

$$a_{\rm Pr} = a_0 = c_0 / \mathrm{S} \tag{vi}$$

The suffix 0 in  $a_0$  and  $c_0$  relates the distance from the corroding face. Now, assuming that  $c_w$ , the hydrogen concentration at the exit face, is zero, then according to Fick's First Law the steady state flux of hydrogen  $J_{\infty}$  $(\text{Ncm}^3. \text{ cm}^{-2}.\text{s}^{-1})^{(3)}$  through the metal is

$$J_{\infty} = D.c_0 / w \tag{vii}$$

where D is the hydrogen diffusivity through the metal (cm<sup>2</sup>.s<sup>-1</sup>). Eliminating c from (v) and (vii), we obtain  $a_{Pr} = J_{\infty}$ w / (D.S). Defining

$$P = D.S$$
 (viii)

in which P (Ncm<sup>3</sup>. cm<sup>-1</sup>.s<sup>-1</sup>. bar<sup>-1/2</sup>) <sup>(4)</sup> is the permeability of hydrogen in the metal, we obtain:

$$a_{\rm Pr} = J_{\infty} w / P \tag{ix}$$

Since S and D vary exponentially with temperature T (K), so does P:

$D = D_0 \exp(-E / RT)$	(x)
$S = S_0 \cdot exp(-E / RT)$	(xi)
$P = P_0 \cdot exp(-E / RT)$	(xii)

P<sub>0</sub>, D<sub>0</sub>, and S<sub>0</sub>, are a pre-exponential factors, R the gas constant (K<sup>-1</sup>) and E (J/mol) activation energies. Grabke and Reicke<sup>16</sup> derived P, S and D for a range of carbon steels. Arrhenius-type plots of D, S and P shown in Figure 3 for a typical steel. Grabke and Riecke's permeabilities for variety of low alloy steels only vary some 20%. As the authors point out, most elements which increase hydrogen trapping causes solubility S to increase, and diffusivity  $D(cm^{-2}.s^{-1})$  to decrease in inverse proportion, and since P = D.S, permeability is not highly dependent on the steel. It is therefore possible to calculate  $a_{\rm Pr}$  from through wall steady state hydrogen flux measurements from (ix) using P values determined from (xii) with a good degree of confidence. In this work and Figure 3 we use permeability values for an average low carbon steel<sup>12</sup> of P<sub>0</sub> 0.00187 Ncm<sup>3</sup>. cm<sup>-1</sup>.s<sup>-1</sup>. bar<sup>-1/2</sup> and E = 34300 J/mol in equation (xii) to obtain:

$$P = 1.76 \text{ x } 10^{6} \text{ exp(-4125/T) pL. cm}^{-1} \text{.s}^{-1} \text{. bar}^{-1/2}$$
(xiii)

Promoting strength  $a_{\rm Pr}$  for a number of important corrodants are presented in Table 1. As mentioned above, entry face hydrogen activities  $a_0$  calculated from hydrogen flux through mild steel are invariant with thickness w – and flux inversely proportional to w - with sour saturated solutions, when w > about 3 mm at 20  $^{\circ}C^{8,9,15}$  and with less promoting solutions, at  $w > 0.5 \text{ mm}^{2,5}$ . However, in much permeation work on sour gas membranes of <1 mm

<sup>&</sup>lt;sup>(2)</sup> In other words, during single face hydrogen charging of steel, if the steel is sufficiently thick for the hydrogen concentration at the surface to be effectively determined by surface reactions, then the surface hydrogen activity at steady state will be effectively the same as would be established through the bulk of steel fully immersed in the same corrodant. Full immersion is more likely to cause hydrogen damage, but that is because hydrogen damage often occurs at the centerline, where, in single face charging scenarios, the hydrogen concentration is half that of the corroding surface, and has one quarter of the cracking propensity.

<sup>&</sup>lt;sup>(3)</sup> 1 Ncm<sup>3</sup>. cm<sup>-2</sup>.s<sup>-1</sup> = 9.44 x 10<sup>8</sup> pL.cm<sup>-2</sup>.s<sup>-1</sup>. Flux J throughout this work is quoted in pL.cm<sup>-2</sup>.s<sup>-1</sup> as more familiar - see also comment (1). 1 pL corresponds with  $10^{-12}$  L hydrogen gas at 20 °C and one atmosphere (1.013 bar). <sup>(4)</sup> 1 Ncm<sup>3</sup>. cm<sup>-1</sup>.s<sup>-1</sup>. bar<sup>-1/2</sup> = 9.44 x 10<sup>8</sup> pL. cm<sup>-1</sup>.s<sup>-1</sup>. bar<sup>-1/2</sup>. See comment (3).

<sup>&</sup>lt;sup>(5)</sup> Bockris (reference 2, Figure 7b) provides data showing the inverse relation between flux and thickness for cathodically polarised membranes down to 0.4 mm thickness in 0.1 N sulfuric acid. The maximum flux is about 50 µA.cm<sup>-1</sup> or 6,500 pL/cm<sup>2</sup>/s. A similar maximum flux is obtained from 1 bar saturated NACE TM0284 solution A though 3 mm membranes at

thickness have been tested. So promoter strengths derived from thin membrane work are less reliable, as, incidentally, will be D and  $c_0$  data obtained from this flux data using (vii). In some otherwise excellent studies, the temperature is not even cited, which is a shame given the variance of all permeation parameters on temperature. Furthermore, in gleaning the literature it becomes apparent that actual flux permeation profiles are rarely presented, and flux data obtained from otherwise identical hydrogen entry regimes are prone to vary radically, contrary to the expectations presented above. In particular, Ni coatings employed at the exit face used for anodic stripping of hydrogen in Devanathan cells appear to retard flux relative to Pd coatings. For all the above reasons, Table 1 data has been carefully selected. A comparison of good (*ie* relatively stable and inter-consistent) Devanathan cell derived flux and flux obtained using the hydrogen collection method, which depends upon hydrogen association and desorption at the exit face, is presented by Kittel *et al.*<sup>8</sup>. Indeed, Table 1 provides a good benchmark for what flux and activities might be expected in different corrosion scenarios. The effect of temperature is explored in the next section.

From Table 1 can be seen that sour gas is probably the strongest promoter. Thiosulfate and sulfite probably form  $H_2S$  cathodically. It is unlikely weak promoters like carbonic acid form hydrides. But notably this, and reportedly weak promoters like ethylenediaminetetraacetic acid (EDTA), sulfuric acid and maleic acid all carry more than one chemically active hydrogen, consistent with the mechanistic view presented in the previous section.

Values of  $a_{pr}^2$  in Table 1 indicate the equilibrium pressure of molecular hydrogen which would be needed to generate the concentration of hydrogen in a metal generated by a particular promoter. So  $a_{pr}^2$  is also the maximum hydrogen pressure that could be generated in a microcrack in the metal because of corrosion involving the promoter, and  $a_{pr}^2$  values provide a direct indication of the potential severity of a promoter containing corrosive solutions, in the field or laboratory, to cause cracking. It should be noted that a strong promoter like sour gas promotes a hydrogen activity in mild steel comparable to the Young's modulus of a typical mild steel ( $\approx 200MPa = 2.10^6$  bar).

#### VARIATION OF HYDROGEN PROMOTER ACTION WITH TEMPERATURE

It is commonly accepted that hydrogen promoted corrosion rarely causes hydrogen induced cracking above about 100 °C, 212 °F, and this makes intuitive sense given that the solubility of hydrogen in steel increases sharply with temperature, Figure 3. So we might expect to see a progressive decrease in the strength of a particular promoter,  $a_{\rm pr}$ , as temperature is decreased. How is this to be quantified? There is very little data in the literature on variance of promoted hydrogen flux with temperature, so we might start with a theoretical basis and then qualify it with practical considerations.

The variation of the logarithm of flux-thickness,  $\log(J_{\infty}w)$ , with T for *unpromoted* corrosion is shown as the lower line in Figure 4. Note  $J_{\infty}w = P a_{pr}$ , equation (ix), and so the unpromoted corrosive permeation line is constructed from (ix) and (xiii) with w = 1 cm  $a_{pr} = 1$  bar at all temperatures. The line supposes sufficient corrosion to cause hydrogen gas saturation of the steel surface (at one bar), and as can be seen some of the high temperature corrosion scenarios this is not the case. For *sour gas promoted* corrosion, a similar Arrhenius dependency is assumed, by the upper line bisecting low temperature sour promoted flux-thickness data, and the flux-thickness for unpromoted corrosion at infinite temperature (1/T = 0). This is indicated by the convergence of the plotted lines in Figure 4. The rationale for this line is in consideration of hydrogen promoters as acting as catalysts which lower the activation energy for hydrogen entry into steel. This lowering of activation energy Ea attending standard sour promoted corrosion, calculated from the gradient of they grey line, is found to be 17 kJ/ mol as compared with 34.3 kJ/mol for unpromoted hydrogen permeation; it is effectively halved. The theoretical maximum flux promotion afforded at any temperature would be given by a similar line of Ea = 4.15 kJ/mol, the activation energy for diffusion through the steel.

 $20 \,^{\circ}$ C (see typical values in Table 1). This is expected, in that the inverse flux thickness relationship depends on the rate of hydrogen permeation – ie flux – being insignificant relative to the rate of hydrogen association, and this condition can be achieved through unpromoted hydrogen entry as much as membrane thinness.

As illustrated,  $a_{pr}$  for sour gas is given by the difference between the two lines, *ie* the ratio of flux generated by one bar of hydrogen gas for which  $a_{pr} = 1$  and flux generated by sour gas. The horizontal line on the graph indicates that sour gas corrosion can generate the same hydrogen permeation as non-promoted hydrogen entry at about 350 °C, and this tallies with high temperature flux data. The sour corrosion measurements by completely different workers at 21 °C °, <sup>10</sup>, and 25 °C, <sup>8</sup>, and a 30 °C, <sup>17</sup>, data points fall on the sour gas promotion line, despite the latter datum relating to 2 bar. The latter may be considered in the light of weak dependency of hydrogen promotion on sour gas concentration, as discussed above. 15 bar H<sub>2</sub>S delivers twice the promotion, in line with this. In summary then, as the temperature is increased, the permeability of mild steel increases rapidly with temperature. However, flux obtained from corroding solutions containing sour gas at a constant partial pressure are only expected to increase slightly, because the promoter's benefit in reducing activation energy of hydrogen entry lessens with increasing temperature (kT). Another consideration is that a sour gas becomes less soluble with increasing temperature.

The variation of sour gas  $(a_{pr})^2$  vs T, derived from  $a_{pr}$  values indicated by the vertical arrow in Figure 4, is shown in Figure 5. This demonstrates explicitly why steel at 100 °C is not liable to sour gas corrosion induced damage. The horizontal arrow shows that sour gas corrosion at 30 °C would generate hydrogen flux though steel of about the same magnitude as flux from unpromoted acid corrosion at 300 °C, say from acidic oil samples. So is found to be the case.

#### VARIATION OF PROMOTION WITH SCALE, COATINGS AND SURFACE CONDITION

Coatings normally act to prevent corrosion and subsequent hydrogen flux in direct proportion. One such metallized coating has been found to do just that in one study of sour induced hydrogen flux<sup>18</sup>.

The situation with scale may be more complicated because there is little doubt that hydrogen promoted flux is due to catalytic surface reactions and that therefore even monolayers of scale, which may support electrochemical corrosion reactions, especially if they are degenerate semiconductors, may not support hydrogen flux entry into steel, either because they are hydrogen impermeable or because they simply do not support the mechanism for hydrogen entry. However, there is to date no direct evidence for this scenario.

Another area deserving further study is the effect of surface condition. In our experience field measured hydrogen flux are never as high as laboratory measured flux. No satisfactory explanation for this can be at present given.

#### CONCLUSIONS

A mechanism for hydrogen flux promotion was proposed which explains why certain elemental hydrides promote corrosion whilst others do not.

The paper provided a parameter, promoter induced hydrogen activity, by which hydrogen promoter strength can be quantified. The measurement enabled experimental values from the literature to be compared. Sour gas was considered the most promoting of all the hydrides. The parameter was also used to assess temperature dependence of hydrogen flux promotion. This treatment confirmed that promoter strength is expected to weaken rapidly with increased temperature, as will cracking severity due to weakened promoter action, at increased temperatures.

# UNAPPABLESOVED

### TABLE 1. SCALE OF PROMOTER STRENGTHS, $a_{\rm Pr}$ , FOR CARBON STEEL AT CITED TEMPERATURES <sup>(6)</sup>

Pro- moter	Solution	w / mm	T/ °C	$I_c / mA.$ $cm^{-2}$	pH (most active)	$J_{\infty}.w/$ pL.cm <sup>-2</sup> .s	$a_{\mathrm{Pr}}$ / bar <sup>1/2</sup> H <sub>2</sub>	$a_{\rm Pr}^2$ / bar H <sub>2</sub>	Ref.
$H_2S$	Sour sat. in 5% NaCl, .4% Na.ac.	10	25	corr	4.5	2273	1174	1,380,000	8
$H_2S$	Reference 25,		21	corr	4.5	1648 1720	1021 1072	1,060,000 1,150,000	10,18
$H_2S$	buffered	16	21	corr	2.7	1308 1313	1197 1252	1,430,000 1,570,000	10
$H_2S$	10% NH <sub>4</sub> OH, 1 bar H <sub>2</sub> S, CN <sup>-</sup> adn		21	corr	~8.4	2155	1410	1,990,000	10
$H_2S$	ASTM <sup>(7)</sup> D-1142 brine +2 bar $H_2S$	8.77	30	corr	~4.5	2481	1020	1,040,000	17
	Ditto, 15 bar H <sub>2</sub> S					7335	3016	9,100,000	17
$H_2S$	1 bar sour sat.				5	417	(860)	(740,000)	
$H_2S$	5% NaCl 1mol/L	1	25	corr	4	480	(991)	(985,000)	11
$H_2S$	ac. buffer				2.5	568	(1175)	(1,380,000)	
HF	Typical field measurements	10	30	corr	4	1000	1150	1,300,000	19
$H_2SO_3$	0.01M in 0.05M		25?	1.25	1.8	53	(850)	(280,000)	20
$H_2S_2O_3$	$\begin{array}{c} H_2 SO_4 + 0.45 \text{ M} \\ Na_2 SO_4 \end{array}$	0.25			1.8	64	(1030)	(190,000)	20
$H_2S$	Na <sub>2</sub> S in var. pH solutions				4.5	-	(1200)	(1,400,000)	5
PH <sub>3</sub>	$Ca_3P_2$ , ditto	(2.5.4)	202	0.5	2.8	-	(1075)	(1,150,000)	5
SeH <sub>2</sub>	NaSeO <sub>3</sub> , ditto	(2.34)	20?	0.5	3.0	-	(975)	(950,000)	5
TeH <sub>2</sub>	Na <sub>2</sub> TeO <sub>4</sub> , ditto				2.2	-	(850)	(750,000)	5
AsH <sub>3</sub>	NaAsO <sub>2</sub> , ditto				2.1	-	(775)	(600,000)	5
$H_2SO_4$	Typical field and lab values		(20)	corr			(100)	(10,000)	(21)
H <sub>2</sub> CO <sub>3</sub>	0.5 g/L NaHCO <sub>3</sub> 5% CO <sub>2</sub>	3	20	corr	7	14	9	84	22
Ac.ac.	acetic acid	6.4	116	corr	~	91	2.4	5.6	24
CPCA	cyclopentane carboxylic acid	6.4	211	corr	~	228	0.6	0.36	24
red crude	TAN 2.3 crude under reflux	6.4	417	corr	~	864	0.33	0.1	24
HCl	1 M HCl	6.4	20	1	1	6	1	1	14,23

<sup>&</sup>lt;sup>6</sup> The data is drawn from steady state flux, or, in the case of reference 5, relative hydrogen saturation concentrations generated in steel by the different promoters tested, using equation (vi). Actual flux-thickness values are reported, but estimated values of  $a_{Pr}$  are shown in parentheses. Allowance being made for thin membranes<sup>5,11,20</sup> on basis of reference 8 data comparing 1 and 10 mm membranes (see text). Some weak and non-promoting corrrodants are shown at the bottom of the table for comparison. <sup>7</sup> ASTM International (ASTM), 100 Barr Harbor Dr., West Conshohocken, PA 19428.





FIGURE 1 - The Periodic Table, showing hydrogen chemistry of the elements. Weak behaviour is annotated by half filling of the element's position. For example, both Al and Ge form molecular hydrides, but also there is some evidence of macromolecular hydrides and the elements are weakly hydrogen permeable. Metals are deemed to exhibit weak hydrogen permeability if permeation rates below about 10<sup>-12</sup> cm<sup>3</sup>. cm<sup>-1</sup>.s<sup>-1</sup>. bar<sup>-1/2</sup> (10<sup>-3</sup> pL. cm<sup>-1</sup>.s<sup>-1</sup>. bar<sup>-1/2</sup>) at 20 °C have been published. This is about the lower permeability limit for austenitic steels. Ferritic steel is about 1000 times more permeable than this, and palladium 10<sup>6</sup> times more permeable. It is remarkable how many metals do exhibit permeability



FIGURE 2 - Promoter mechanism on steel, shown as a sequence (1) to (3). Hydrogen sulfide action is shown on the left, hydrogen fluoride on the right. Note how the intermediates, shown in (2), resemble the promoter hydride. Note also the hydrogen entering the metal is originally attached to the promoter, not to the steel surface



FIGURE 3 - Permeability P, diffusivity D and solubility S of hydrogen in steel variation with temperature using data for a typical steel from reference 16 ('St0', table 1). Note according to the McNabb trap model used in ref. 16, and the data presented, traps do not impact on the permeability of hydrogen through steel



1000/T / K

FIGURE 4 - Hydrogen promotion *vs* temperature. Lines are theoretical, for unpromoted flux generated by a corrodant producing 1 bar molecular hydrogen ( $a_{Pr}=1$  bar<sup>1/2</sup>), and for sour gas, at its activity at 25 °C ( $a_{Pr}=1200$  bar<sup>1/2</sup>). See text for explanation of dashed lines and arrows. Legend refers to 1 bar H2S and reference 15 <sup>(8)</sup> solution A unless otherwise specified

<sup>&</sup>lt;sup>8</sup> National Association of Corrosion Engineers (NACE) TM0284 solution A.



FIGURE 5 - Calculated plot of hydrogen cracking severity,  $(a_{Pr})^2$  vs T for sour solution of sour corrosion severity obtained by sour saturated reference 25 solution at 25 °C. In practice the cracking severity is usually lower as sour gas becomes decreasingly soluble with temperature. The graph shows clearly why hydrogen damage rarely occurs at elevated temperatures

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