

Converting hydrogen flux to corrosion rates and hydrogen crack risk

Introduction

Hydrogen flux measurement provides a useful measure of corrosion, in circumstances where flux is an inevitable consequence of an active corrosion scenario, and where there are substantial savings to be obtained in measuring changes in corrosion activity over relatively short time intervals.

Key applications are

- Distillation unit overhead corrosion assessment¹
- Amine salt deposit corrosion mitigation¹
- Cyanidic ammonium bisulfide corrosion assessment
- HF corrosion control²
- High temperature corrosion measurement and control^{3,4}
- Hydrogen crack risk in sour systems^{5,6}
- Hydrogen bakeout monitoring⁷

In all these applications flux measurements provide a comparator of active corrosion, which can be used to improve oil production and processing. It is usually desirable to obtain from the flux a quantitative estimate of active corrosion rates and hydrogen damage risk.

The scientific basis for the correlations presented below are discussed in detail elsewhere^{4,6}. In brief, acid corrosion can generate hydrogen activity just under the corroding surface. The hydrogen flux which permeates the steel depends on this activity, the steel thickness and hydrogen permeability, which is temperature dependent. It has been shown that crack susceptible and crack resistant steels⁵ and other variously prepared steels⁸ do not vary significantly in their hydrogen permeability. It is also now well demonstrated that flux varies inversely with steels of >5 mm thickness⁹⁻¹¹. So from a flux measurement, steel thickness, steel temperature and permeability data⁸, we can work out hydrogen activity, 'normalised' for thickness and temperature, and thus potentially closely correlated with crack risk and corrosion rate.

Hydrogen activity can be expressed as an equivalent pressure of molecular hydrogen, and provides a direct measure of the hydrogen cracking risk posed by active corrosive hydrogen flux.

In the case of flux through steel subject to acid corrosion at high temperatures, defined here as >100 °C, 212 °F, correlation between flux and activity has also now been clearly demonstrated^{3,4}.

Flux from low temperature corrosion depends on 'hydrogen promoters'. In a recent paper¹² it was shown that this hydrogen promotional effect weakens with increased temperature, thus offsetting the increase in flux expected from increased hydrogen permeability at increased temperatures. The net effect of increased temperature (at constant corrosion rate) is expected to be a weak increase in hydrogen flux.

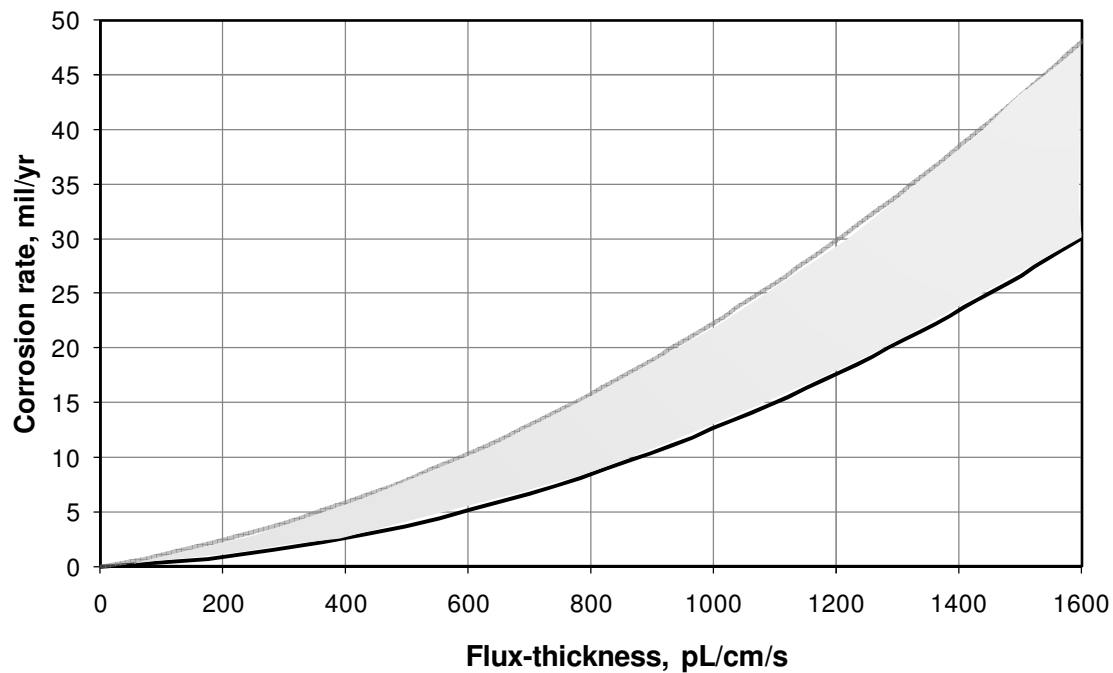
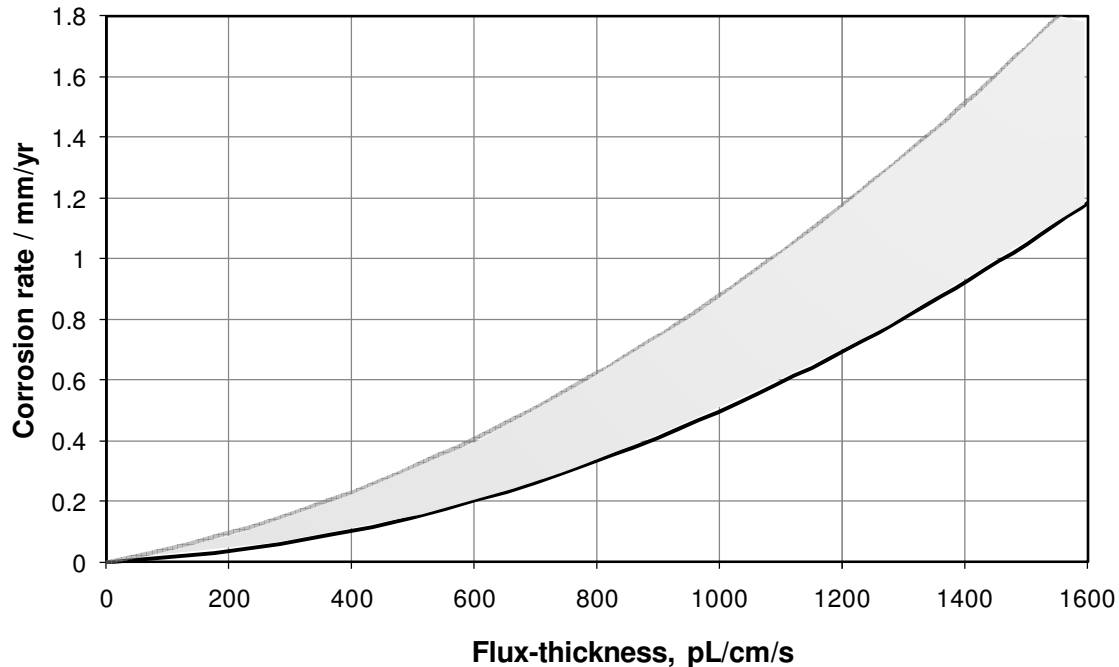
Nevertheless, in all field corrosion scenarios flux is expected to be inversely proportional to thickness, so that is our starting point for converting flux into corrosion rates and crack risk. To obtain the flux-thickness, multiply flux in pL/cm²/s by test site thickness in cm. eg, for a flux of 20 pL/cm²/s through ½ in steel wall = 1.5 cm => flux-thickness = 30 pL/cm/s. In the charts below, the flux thickness should be found on the horizontal axis. The approximate corrosion rate is indicated directly above the flux-thickness.

Sour corrosion rates

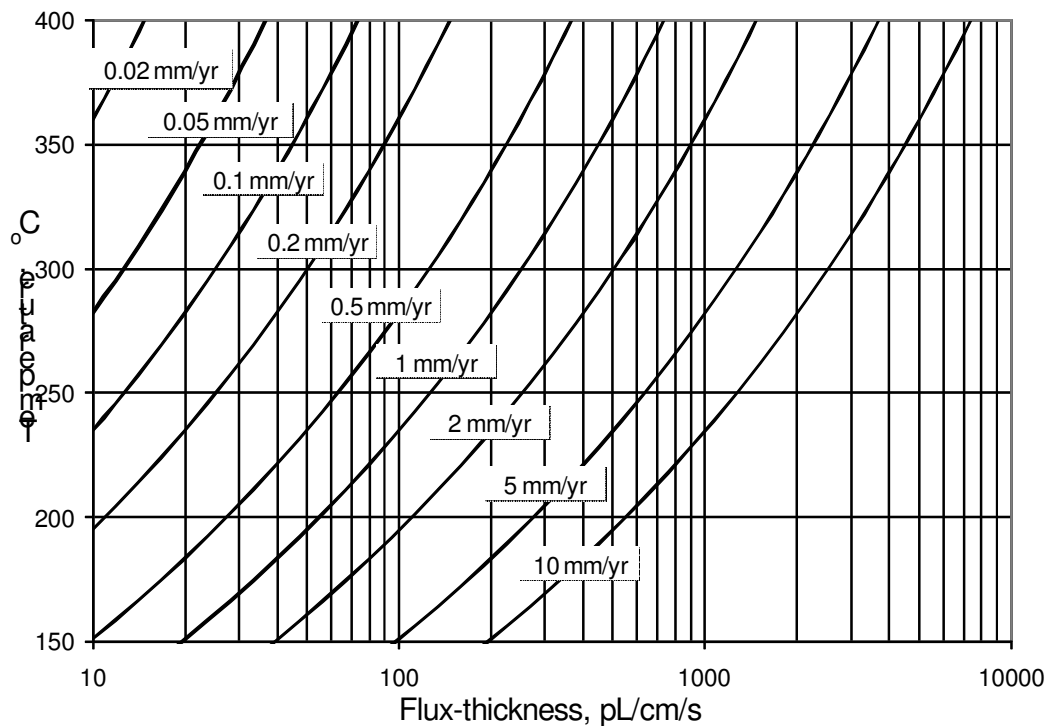
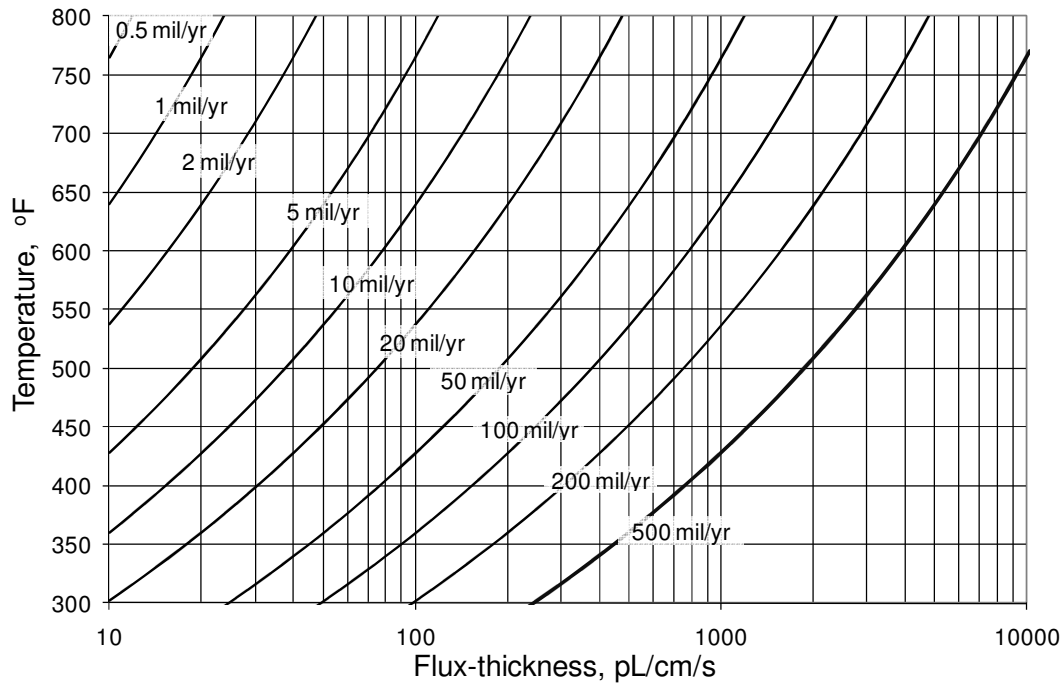
Typical application sites for sour corrosion flux measurement are overheads, condensers, fin-fan units, coolers and sour flare lines. Sour corrosion can be very severe and is often associated with hydrogen damage (see *Hydrogen damage risk* below). It is usually more episodic than is realised, occurring only, for example, immediately after equipment installation, internal inspection, or during process changes (eg air ingress, water washes, pH changes).

Hydrogen flux is not particularly sensitive to pH or concentration of sulfide in the liquid phase. This is evident from measurements of quite significant hydrogen flux due to corrosion under salt deposits, eg in sour gas lean amine lines. Also, the correlation applies to cyanidic ammonium bisulfide, which occurs in overhead streams from hydrodesulfurization columns, hydrotreaters and catalytic crackers, where hydrogen cyanide is present from high nitrogen containing feedstock.

Sour corrosion rates can be confidently predicted from flux *only if* the corrosion is contingent upon removal of corrosive scale to reveal bare steel. The correlation indicated in the chart is based on laboratory experiments⁵ and field experience with scale free steel in the range of 5-50 °C, 40-120 °F. More confident correlation can be expected by direct comparison of averaged flux with wall loss data over the same period, in specific scenarios. It should be noted that sour corrosion is far more episodic than commonly realized (wall loss measurements providing an average over long times). The upper boundary for the corrosion rate estimates shown below is less well defined than the lower boundary.



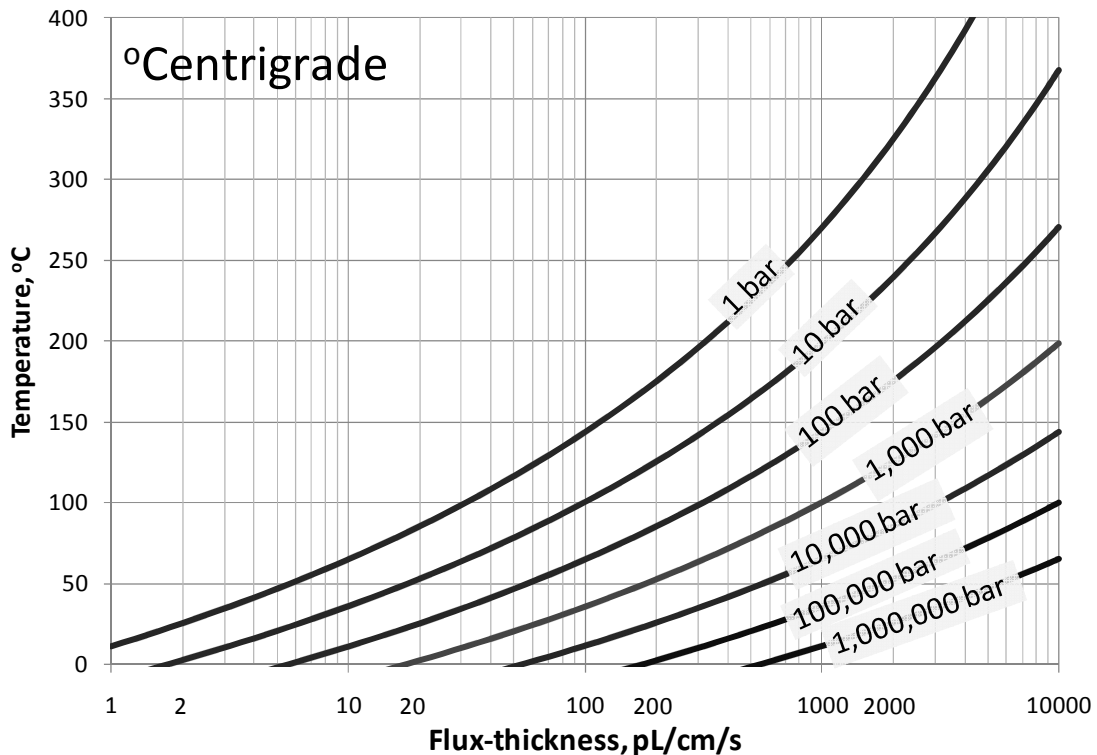
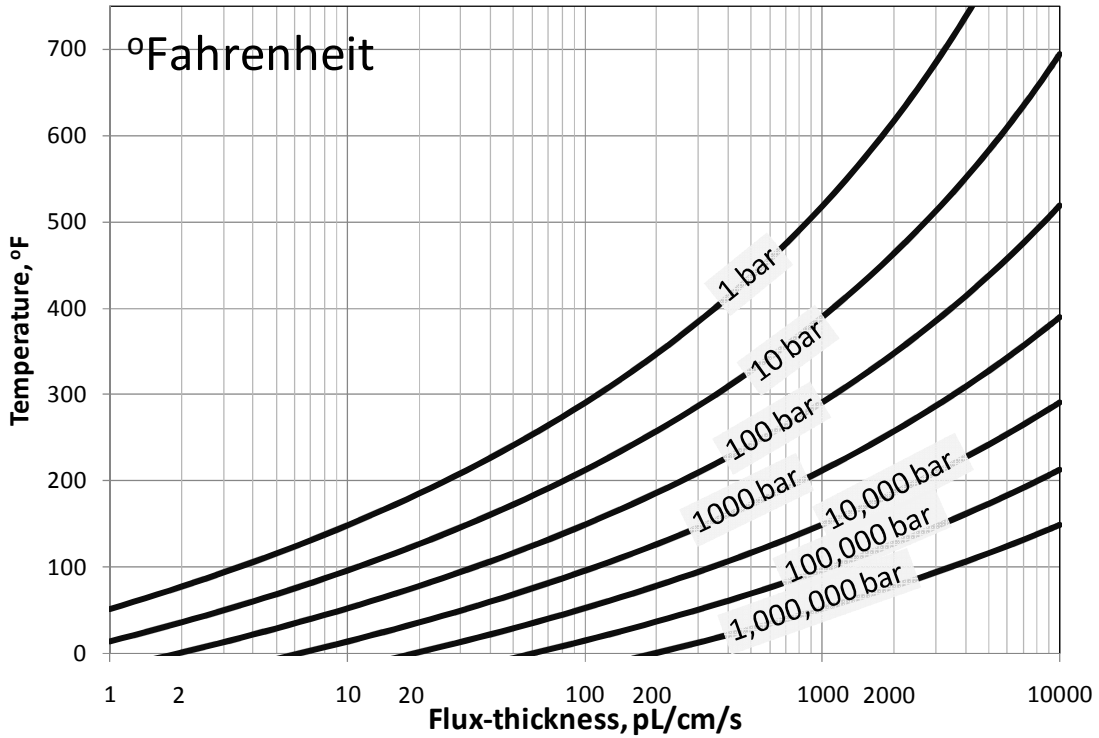
High temperature acid corrosion



The best known high temperature corrosion is due to 'naphthenic acid', in fact a variety of organic acids found in crude oil. Corrosion generally occurs at pipe bends and reducer sections. The correlation below is based on lab experiments and some field data^{3,4}. The chart is also applicable to other acidic corrosion above about 150 °C, 300 °F. Please contact Ion Science for further technical information.

To use the charts, look up the flux-thickness on the horizontal axis, then the temperature on the vertical axis (*top*, °F, *bottom*, °C). The estimated corrosion rate is shown. Corrosion rates for 5 Cr steel are expected to be approximately double those indicated by the chart.

Hydrogen crack risk



Corrosion of carbon steel in sour, cyanidic bisulfide and HF service can generate high hydrogen activity in affected steel. This activity determines the hydrogen flux generated through the steel. Also, expressed in bar, the activity is a direct measure of crack severity. To obtain hydrogen crack risk, first determine the hydrogen activity with the charts above (*top*, °F, *bottom*, °C) by looking up the flux-thickness of the service steel on the horizontal axis, and temperature on the vertical axis. From this hydrogen activity and the table overleaf to determine the hydrogen damage steel.

Carbon steel quality:	Is steel more than 18 mm thickness?	activity a_0		
		100 to 10,000 bar	10,000 to 1,000,000 bar	More than 1,000,000 bar
Poor steel, or steel poor weld HAZ	yes	2	3	3
	no	1	2	3
Average steel, or good weld HAZ	yes	1	2	3
	no	0	1	2
sour service	yes	1	1	2
	no	0	0	1

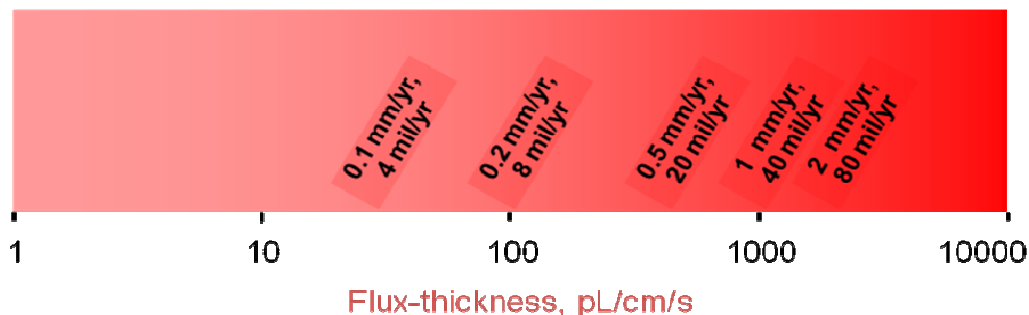
Table hydrogen damage risk: 0 = zero, 3 = high

Key risk factors:

- 0: No risk of active damage at site of measurement.
- 1: Small risk of crack initiation, some risk of crack propagation, especially in steel known to be susceptible.
- 2: Moderate risk of crack initiation. Likely crack propagation.
- 3: High risk of crack initiation and certain crack propagation.

Standard NACE TM0284 generates an activity of about 1,300,000 bar. Generally, hydrogen cracks are initiated in poor quality, non-sour service steels, and welds, at activities as low as 10000 bar, whereas sour service steels can withstand at least 1,000,000 bar. After cracks have appeared, much lower activities are needed to propagate them, indeed, any flux may contribute to further crack growth. In order to ensure close correspondence between flux measurements and active corrosion, it is recommended that measurements are carried out on unblistered steel.

HF Corrosion



HF is used to catalyse the formation of branched C8 olefins from smaller olefins. The alternative catalyst – sulfuric acid – also causes corrosion but provides a much weaker flux signal. HF corrosion is very widespread and continuous. There is probably some temperature dependency for corrosion-flux correlation not shown on the chart. From hydrogen flux measurements it is evident that HF alkylation unit corrosion is generally more extensive and continuous than sour corrosion.

Notes

Data presented in this document is intended to provide an indication only of corrosion rate and hydrogen damage risk, on the basis of correctly carried out hydrogen flux measurement with calibrated Hydrosteel equipment. No responsibility can be accepted by Ion Science Ltd for damage or injury caused by use of information contained herein.

A further update is planned for 2012-3 at which time it is likely that correlations of corrosion rate in HF and specific sour scenarios will be further refined.

Ion Science welcomes your comments regarding the information contained in this document.

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F.W.H.Dean, 14 June 2010