Converting hydrogen flux to corrosion rates and hydrogen crack risk

Introduction

Hydrogen flux measurement provides a useful measure of corrosion, if flux is an inevitable consequence of an active corrosion scenario, and when it is useful to know about changes in corrosion activity over relatively short time intervals.

Key applications are
- Distillation unit overhead corrosion assessment[1]
- Amine salt deposit corrosion mitigation[1]
- Cyanidic ammonium bisulfide corrosion assessment
- HF corrosion control[2]
- High temperature corrosion measurement and control[3,4,5]
- Hydrogen crack risk in sour systems[6,7]
- Hydrogen bakeout monitoring[8]

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[4,5,6]. 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. It has been shown that crack susceptible and crack resistant steels[7] and other variously prepared steels do not vary significantly in their hydrogen permeability. It is also now well demonstrated that flux varies inversely with steels of >5 mm thickness[10-12]. So from a flux measurement, steel thickness, steel temperature and permeability data[9], 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 been demonstrated[3,4].

Flux from low temperature corrosion depends on 'hydrogen promoters'. The hydrogen promotional effect appears to weaken[12] at 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 .

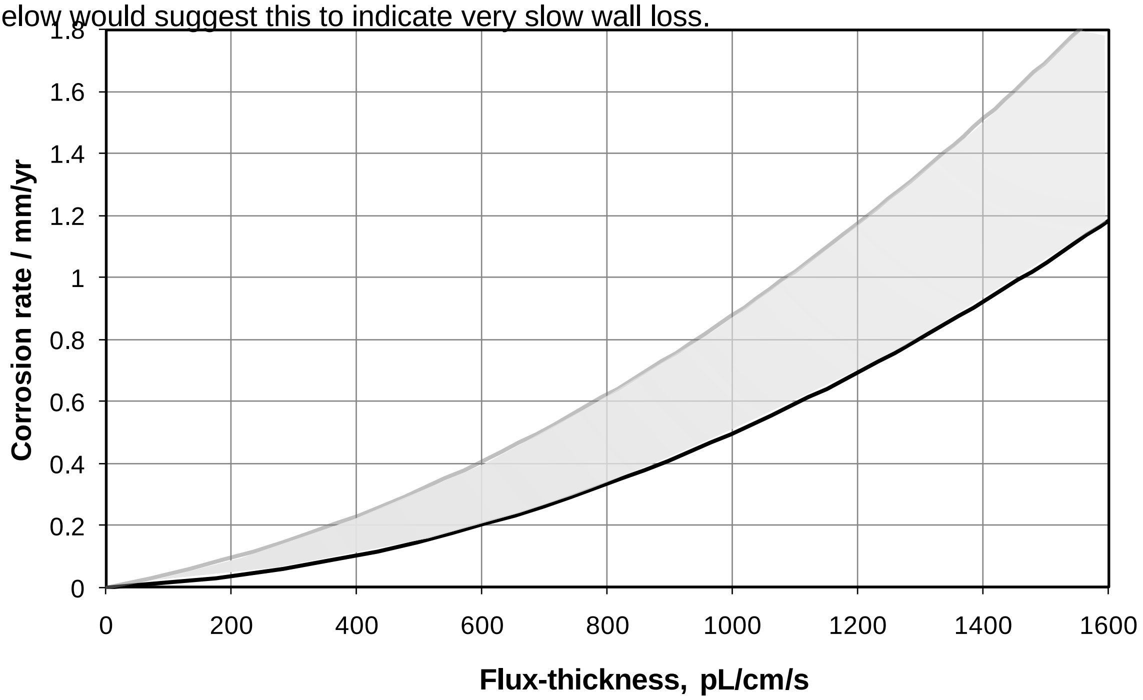
Nevertheless, in all field corrosion scenarios flux is expected to be inversely proportional to thickness, so that is our starting point for converting flux into corrosion rates and crack risk. To obtain the flux-thickness, multiply flux in pL/cm^2/s by test site thickness in cm. *eg*, for a flux of 20 pL/cm^2/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.

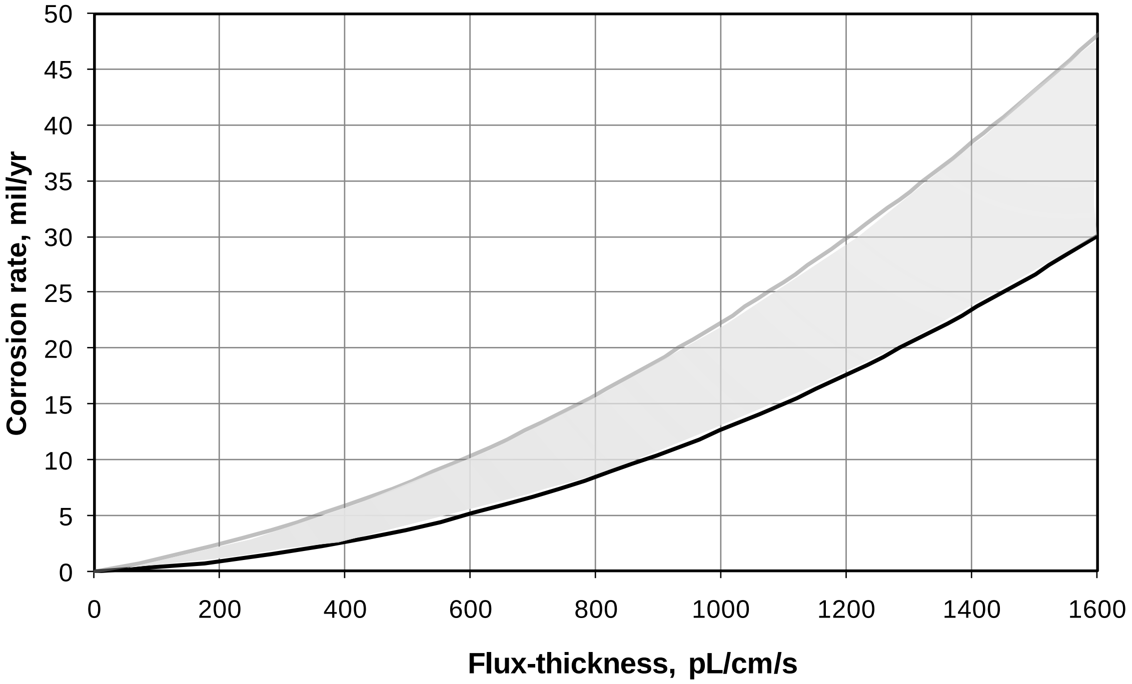
Sour corrosion rates

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, after equipment installation or 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.

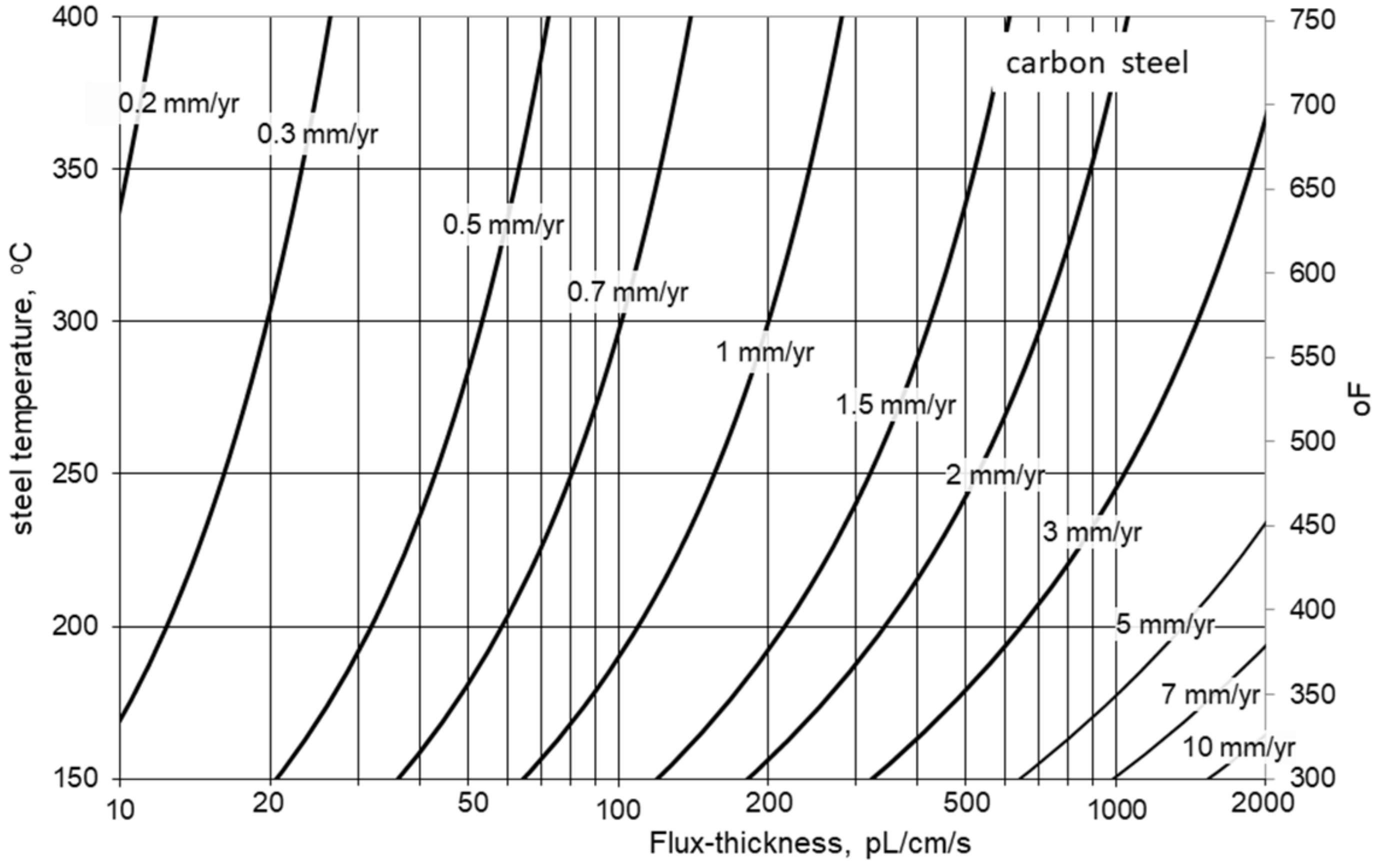
Sour corrosion rates can be confidently predicted from flux *only if* the corrosion is contingent upon removal of corrosive scale to reveal bare steel. The correlation indicated in Conversion 1 is based on laboratory experiments[5] and field experience with scale free steel in the range of 5-50 °C, 40-120 °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. Also, in many field scenarios, flux as low as 10 pL/cm^2/s are considered significant, though the conversion below would suggest this to indicate very slow wall loss.

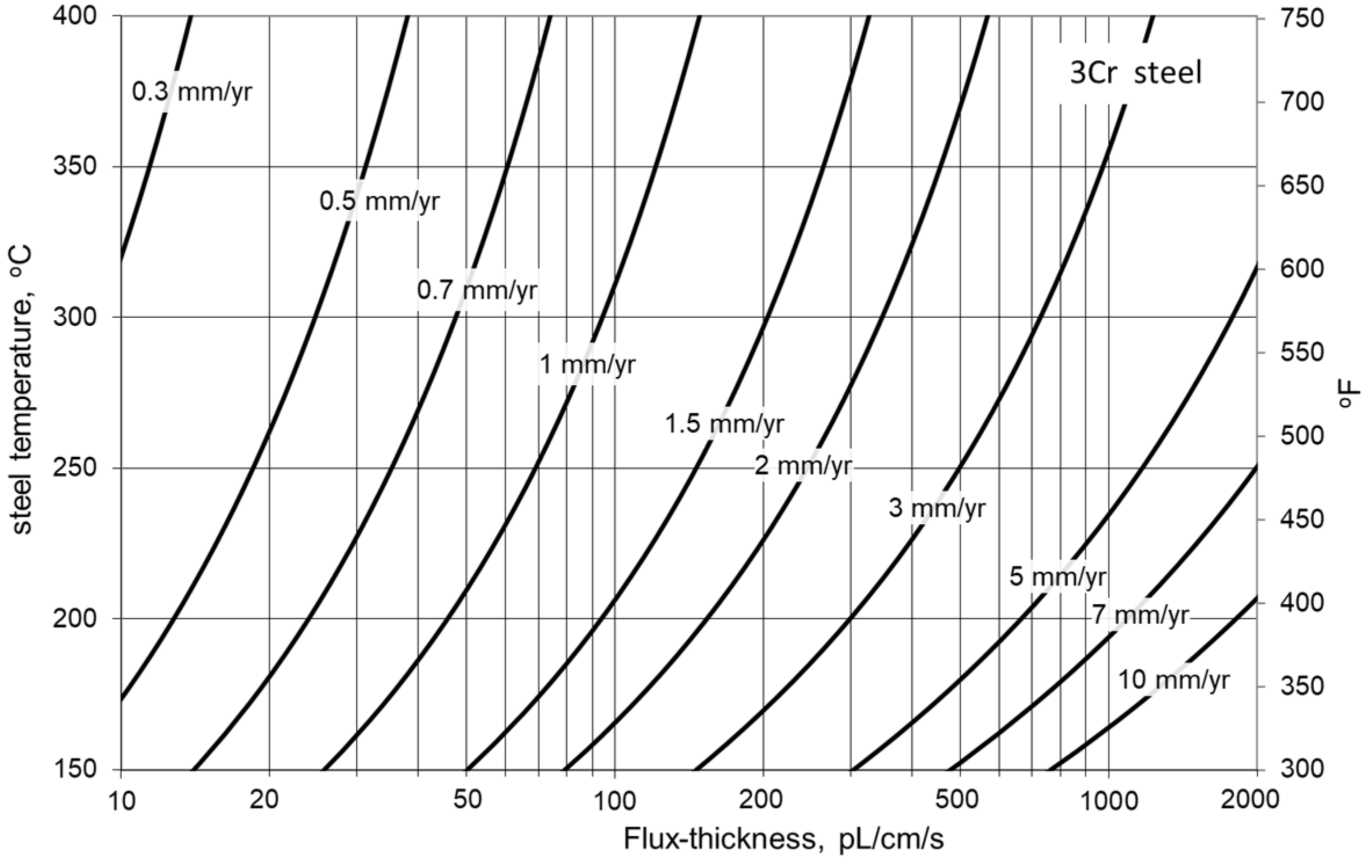


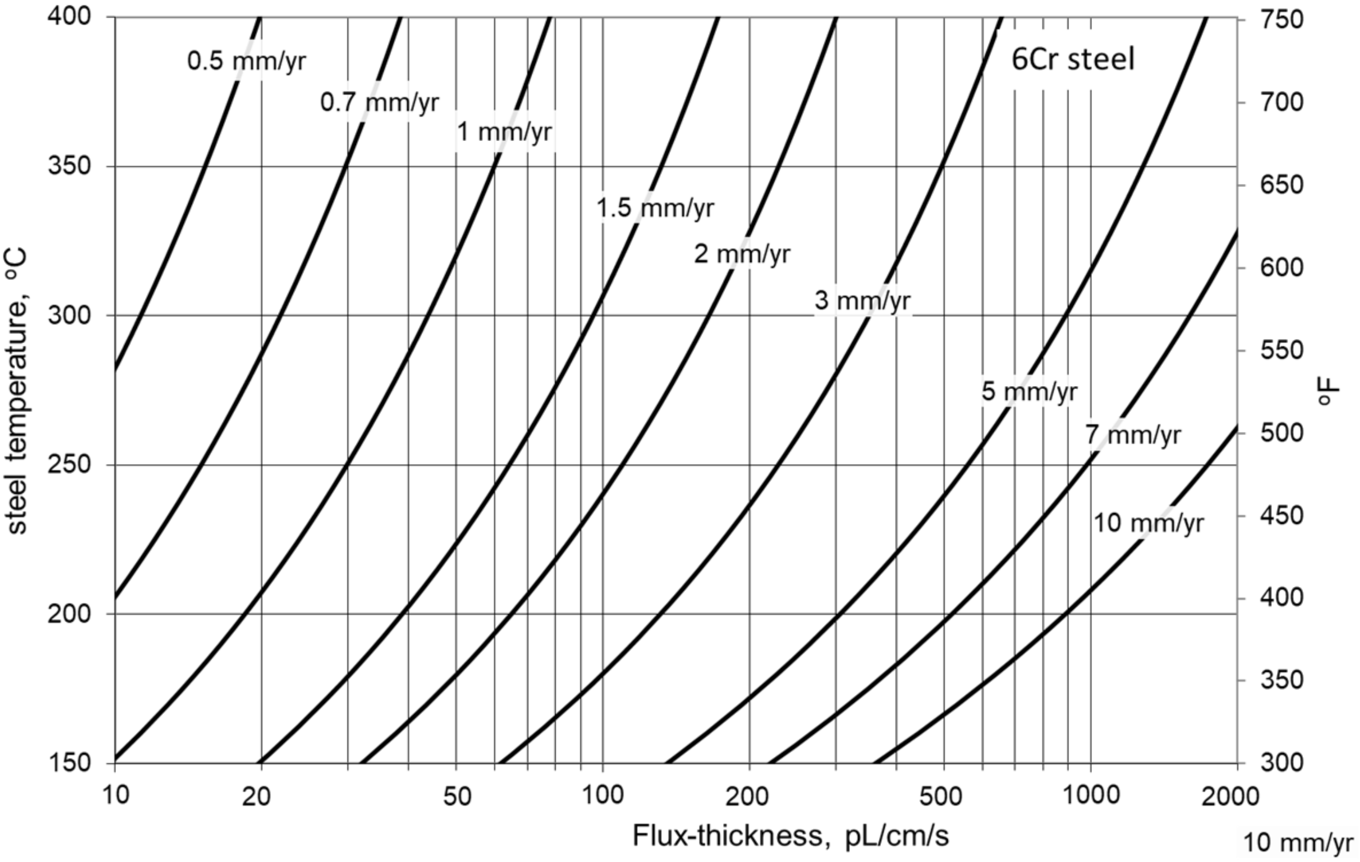


Conversion 1. Sour corrosion of carbon steel. Top: corrosion rate in mm/yr. *Bottom:* rate in mil/yr.

High temperature acid corrosion





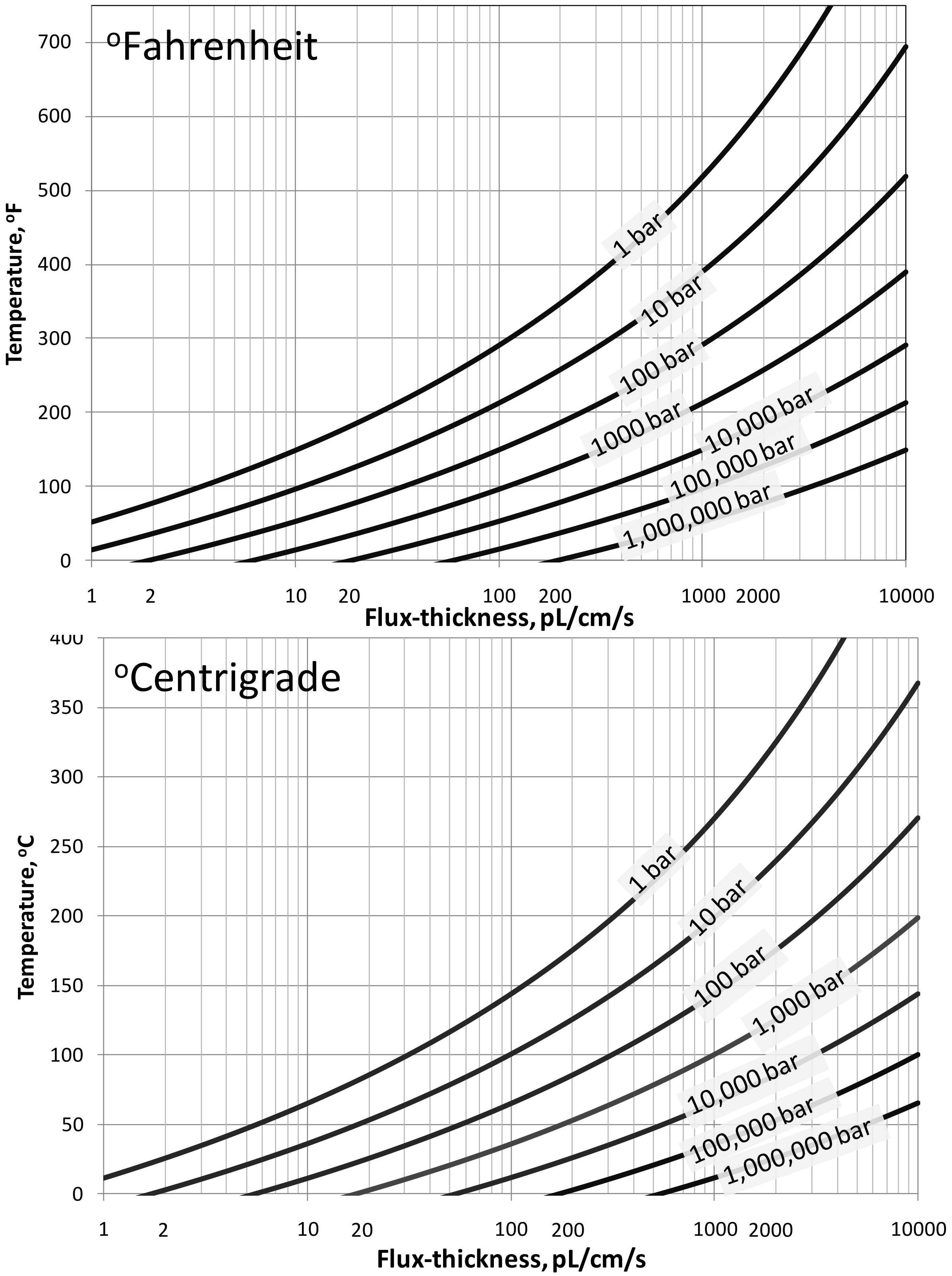


Conversion 2. High temperature acid corrosion of carbon steel, 3 Cr and 6 Cr steel. See text for details.

The best known high temperature corrosion is due to ‘naphthenic acid’; a variety of organic acids found in crude oil. Corrosion generally occurs at pipe bends and reducer sections. Conversion 2 charts based on lab experiments and some field data[3,4]. The chart is also applicable to other acid and water corrosion above about 150 °C, 300 °F, notably high temperature high pressure water corrosion. Allowance has been made for losses of hydrogen flux exiting steel into air[5].

Conversion charts are provided for carbon steel, and 3 and 6 Cr steel, allowing for the effect of alloy content on hydrogen permeability. Ensure you have identified the appropriate chart, then look up the flux-thickness on the horizontal axis, then the temperature on the vertical axis (°F or °C). The estimated corrosion rate is shown.

Hydrogen crack risk



Conversion 3. Hydrogen activity used to assess hydrogen crack risk. Top: °F. *Bottom:* °C.

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 obtain the hydrogen activity from Conversion 3 by looking up the flux-thickness of the service steel on the horizontal axis, and temperature on the vertical axis. Use this hydrogen activity in Table 1 below to determine the hydrogen damage risk to steel.

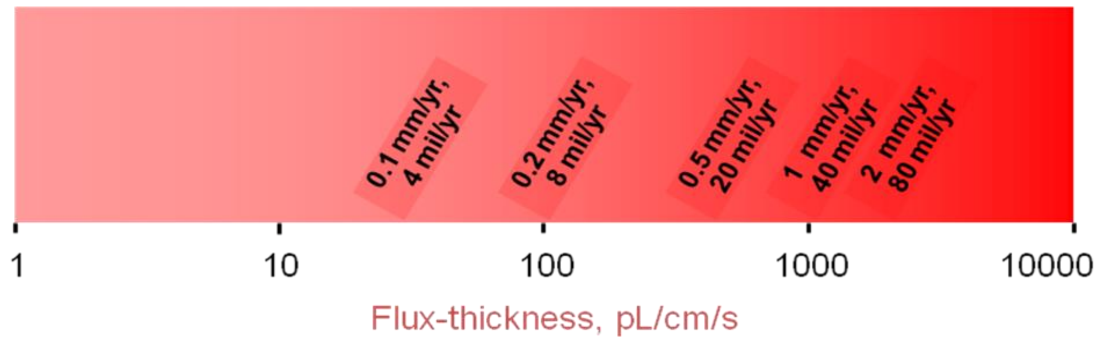
		activity a_0			
Carbon steel quality:	Is steel more than 18 mm thickness?	5 to 100 bar	100 to 10,000 bar	10,000 to 1,000,000 bar	More than 1,000,000 bar
Legacy steel, steel previously HIC damaged	yes	*1*	*2*	*3*	*3*
	no	*1*	*1*	*2*	*3*
Sweet service steel, or good weld HAZ	yes	*1*	*1*	*2*	*3*
	no	*0*	*0*	*1*	*2*
sour service steel	yes	*0*	*1*	*1*	*2*
	no	*0*	*0*	*0*	*1*

Table 1 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 of crack susceptible steel.
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 10,000 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 measured flux is strongly indicative of 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



Conversion 4. 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 considered in the conversion. From hydrogen flux measurements it is evident that HF alkylation unit corrosion is generally more extensive and continuous than sour corrosion.

Pre-weld Hydrogen Bakeouts

It is often advisable to heat treat equipment under repair, which may have been liable to hydrogen uptake during service, prior to welding. Otherwise trapped hydrogen may concentrate at and near the weld pool, and upon cooling, the weld may fail due to stress oriented hydrogen induced cracking (SOHIC). The time required for such bakeouts cannot be confidently defined, as in one instance there may be little trapped hydrogen in the steel, in which case the heat treatment can be curtailed, and in another the hydrogen may be held in deep traps, and require an extended bakeout time. Flux monitoring of bakeouts provides an immediate view of the need or otherwise for continued heat treatment. The total hydrogen per unit area released from one face is given by the sum of the flux over time, $\sum J(t)$, in units of pL/cm^2. Assuming the hydrogen releases equally from each side of the steel centerline, the concentration of hydrogen liberated from the steel of thickness w during a bakeout is then $2/w.\ 10^{-9} \sum J(t)$ mL/cm^3 or $2.24\ 10^{-8}/w.\ \sum J(t)$ ppm . 1 ppm hydrogen in carbon steel is considered a possible SOHIC risk, corresponding to a flux of 12,000 pL/cm^2.s for 3 hr from 5 cm thick steel. This magnitude of hydrogen outgas is frequently encountered and confirms the bake out as having been very necessary.

We recommend flux monitored bake outs as being complete upon confirmation of decreasing flux readings <1000 pL/cm^2/s being obtained at the bakeout temperature from all monitored sites. The author notes that deeply trapped hydrogen struggling to escape substantially empty trap sites is probably benign as it will not migrate appreciably to the weld pool. Thus 3000 pL/cm^2/s after 8 hr heat treat from 5 cm steel is considered to present no subsequent SOHIC risk.

Note

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

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