

**CORRELATION OF HYDROGEN FLUX AND CORROSION RATE MEASUREMENTS
CARRIED OUT DURING A SEVERE EPISODE OF CORROSION-EROSION ATTRIBUTABLE
TO NAPHTHENIC ACID**

J.M.O'Kane, T.F.Rudd, J.H.Harrison
Chevron Limited
Pembroke Plant
Pembroke, Wales,
SA71 5SJ
UK

S.J.Powell, F.W.H.Dean
Ion Science Limited
The Way, Fowlmere
Cambridgeshire
SG1 7U J
UK

ABSTRACT

Over a six month period, UT measurements at a matrix of measurement sites on a Fractionation column indicated that it was suffering from severe internal corrosion. It was decided to monitor hydrogen flux at all measurement points on a frequent basis. The resulting flux profiles broadly co-trended. Time averaged flux and longer term corrosion rates correlated well. In a more sophisticated treatment, flux data was converted into hydrogen activity at the corroding face, to compensate for hydrogen permeation through the steel, thus normalising any variations in steel temperature and thickness. Again the correlation of activity and shorter term corrosion rate was good, with a correlation factor that was closely comparable to that obtained from laboratory data. In short, the data illustrates that, at temperatures where naphthenic acid corrosion can take place, hydrogen flux may provide a keen indication of the corrosion rate in near real time, with the diffusive delay in flux stabilization upon a corrosive change typically being one hour.

Keywords: naphthenic acid corrosion, hydrogen flux, visbreaker.

INTRODUCTION

Hydrogen flux monitoring at high temperatures has only been carried out in the field since 2002¹. In particular, the technique has proven with the authors to be highly effective in the monitoring of the need for, effectiveness and completion of hydrogen bakeouts. In this paper and a contemporary paper, we report upon a case of naphthenic acid corrosion (NAC) in an oil refinery visbreaker fractionator, which was monitored over time using hydrogen flux measurements². In this paper, we will concentrate on correlation of the corrosion with the flux. Specifically, we will consider the errors and assumptions associated with every step in the sequence from the generation of

naphthenic acid corrosion through to the recording of a measurement of a high temperature hydrogen flux. By this means, we will know how confident we can be in assessing NAC from flux measurements and how the correlation between the two should be qualified.

The sequence of chemical reactions and movements of the hydrogen atom leading to flux measurement of NAC is depicted in Figure 1. These can be summarized as follows:

1. Corrosive formation of hydrogen on a corroding steel surface
2. Hydrogen entry into the steel wall
3. Hydrogen permeating the steel wall
4. Hydrogen exit onto an external steel surface
5. Hydrogen association and desorption on the external surface
6. Hydrogen flux measurement.

FORMATION OF ATOMIC HYDROGEN IN STEEL

During NAC, naphthenic acid, represented as NpCOOH , is considered to physically adsorb on steel (i), then chemically react, (ii):



The subscript ‘ads’ is used to depict chemical adsorption. It has been suggested that corrosion reaction (ii) could proceed electrochemically. However, given the very low conductivity of production fluids subject to NAC, any anodic and cathodic reactions would have to take place over very small distances, and therefore it is almost certain that, during NAC, hydrogen only forms on steel according to (i), (ii), and not through any semiconducting product layer. We will further assume that hydrogen atoms are formed on the surface of the steel in stoichiometric proportion to the oxidation of the steel, *ie* two H_{ads} per Fe atom.

This is a crucial assumption affecting directly the correlation of flux with corrosion. Are there any ways in which iron could be oxidized or removed, or hydrogen formed, other than by equation (ii)? NAC is specific to locations where the shear velocity of the process stream is sufficient to erode away corrosion product to reveal more steel by which corrosion can progress. Thus for example, corrosion in the visbreaker fractionator was most severe at the splash zones². Erosive iron loss has not been reported in situations where NAC has been eliminated with a suitable corrosion resistant alloy.

Other acid corrodants such as H_2S and mercaptans will produce hydrogen and consume iron in the same proportion as in (ii). However, a process stream containing hydrogen could deliver hydrogen flux without iron loss:



In the visbreaker fractionator, as in other NAC locations, the only source of hydrogen in the process stream was likely to be from cracking of hydrocarbons. In the case of the visbreaker, we estimated a maximum partial pressure of 0.1 mbar hydrogen, in view of the extremely short residence times of fluids expected within the fractionator. The maximum hydrogen activity in steel, a_{process} , caused by equilibration of this process hydrogen through equilibration of reactions (iii), (iv) and (vi) (see below), was then $0.01 \text{ bar}^{1/2}$, delivering a flux of a few $\text{pL}/\text{cm}^2/\text{s}$ at 200°C through steels of typical thickness. The effect was therefore discounted.

HYDROGEN PERMEATING STEEL

Adsorbed hydrogen, H_{ads} , either associates to form molecular hydrogen (v), which desorbs as hydrogen gas, or enters steel H_{Fe} in (vi):





Hydrogen entering the steel by (vi) diffuses through the wall, emerging at the external surface of the steel and exiting into air:



To obtain a correlation between flux and corrosion rate, one must reconcile the relative rates of hydrogen entry and dissociation from (v) vs (vi). At low temperatures, it has been established that at steel thicknesses greater than a few millimeters, steady state flux J_{ss} ($\text{pL.cm}^{-2}.\text{s}^{-1}$) varies in inverse proportion with steel thickness w (cm)^{3,4,5}. This is because the flux of hydrogen entering steel at the corroding surface (vi) and exiting at the external surface in (vii) is sufficiently low for it not to effect the concentration of H_{ads} at the corroding surface. Under these conditions, the hydrogen flux is determined by the permeability P ($\text{pL.cm}^{-2}.\text{s}^{-1}.\text{cm.bar}^{-1/2}$) of hydrogen through the steel:

$$J_{ss} = P.(a_0 - a_w) / w \quad (\text{ix})$$

where a_0 and a_w ($\text{bar}^{1/2}$) are the activities of hydrogen just under the corroding face and external face respectively. With the assumption that a_w is zero, this simplifies to

$$J_{ss} = P.a_0 / w \quad (\text{x})$$

The permeability of steels was investigated by Grabke and Riecke⁶. We adopt their value for mild steel from which the fractionator walls were fabricated,

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

T is the steel temperature (K). Riecke and Grabke's data suggests that variance in mild steels should not cause permeability to vary more than $\pm 10\%$. Adjusted values of the pre-exponential in (xi) are required for chrome alloy steels typically used in high temperature service, for 10% Cr being about half that of mild steel⁶.

Activity a_0 is 'normalized' for the effect of steel thickness and temperature and can be derived from field measured and experimentally determined parameters in (x) and (xi). Does it correlate closely with the rate of high temperature corrosion? Two of the authors extended previous laboratory work on flux measured through steel subject to high temperature acid corrosion using for the most part refinery process samples⁷. Data is presented in Figure 2. A fairly linear relationship is established between activity and corrosion rate, which was particularly satisfactory given the range of test temperatures. The correlation

$$C = 5.2 a_0 \quad (\text{xii})$$

is shown by a solid line, and was adopted in this work and in a contemporary paper. Equation (xii) overestimates the corrosion rate as obtained from the laboratory data, but was considered applicable to field measurements.

HYDROGEN EXIT AND DETECTION

Electrochemical flux measurement technologies based on the Devanathan cell anodically strip H_{ads} from the surface of steel fluxing hydrogen, but these devices are not workable at high temperatures. In this work a flux monitor was employed which engaged the hydrogen collection method⁽¹⁾, which requires hydrogen desorption (xiii) for flux measurement.



⁽¹⁾ Hydrosteel 6000 hydrogen flux monitor, Ion Science Ltd, UK

The external surface of the visbreaker, being exposed to air, would be coated with oxide, affecting the exit of hydrogen in several ways. Firstly, the surface and oxide is liable to contain many trap sites for both surfacing hydrogen, H_{ads} (vii), and $H_{2(ads)}$. By carrying out surface treatments on the exit surface of steel whilst fluxing hydrogen, it has been shown that, at room temperature, such traps, when freshly generated, adsorbed a few $\mu\text{L}\cdot\text{bar}/\text{cm}^2$ of hydrogen⁸. Their occupancy and thus influence on retarding hydrogen flux was however transient and would be less at higher temperatures. Nevertheless, in field measurements on the fractionator, surface abrasion was avoided.

Only H atoms, not H_2 , are expected to penetrate an epitaxial oxide such as chromia on 5Cr steel. The effect can be considered as a permeation barrier equivalent to a thickness of steel, estimated from lab work to be ~ 0.1 cm at 200 °C on 5 Cr steel. However, on mild steel from which the fractionator was fabricated, no such epitaxial oxide would be expected, and the effect was considered negligible.

However, the rate of hydrogen association according to (viii) is second order with respect to $[H_{ads}]$ and therefore there is some non-zero hydrogen activity expected at the exit face. At 20 °C, distortion of diffusion profiles of hydrogen flux through steel was considered significant at < 50 $\text{pL}/\text{cm}^2/\text{s}$ ⁹. Given the much increased rate of (viii) to be expected at > 100 °C, a maximum figure of $a_w = 0.02$ $\text{bar}^{1/2}$ is likely for high temperatures, which effectively would double the estimated corrosion rate at a measured flux of 6 $\text{pL}/\text{cm}^2/\text{s}$ at 200 °C. Therefore, high temperature corrosion rates estimated from flux of less than 10 $\text{pL}/\text{cm}^2/\text{s}$ were treated cautiously.

A further consideration at the exit face is that atomic or molecular hydrogen might be oxidized instead of desorbing through (viii) and (xii). The extent to which this happens is not known, but it is noted that the auto-ignition temperature of hydrogen and oxygen is about 500 °C, and oxide at the exit face is unlikely to provide a suitable substrate for this reaction. We estimated 5% loss of hydrogen to oxidation for steel at 200 °C, the typical skin temperature of measurements on the visbreaker fractionator.

Finally, we consider the actual flux measurement. The apparatus is described elsewhere⁹. During the measurement epoch it was occasionally checked with a calibration check device and confirmed it to be accurate to within $\pm 5\%$. However, this did not reveal the collection efficiency of the particular 60 mm ‘roaming’ probes⁽²⁾ used in capturing hydrogen flux, which in the field was liable to raise a number of measurement uncertainties. The uncertainties were based upon operation staff, trained in field flux measurement:

1. After the probe was attached to steel and at a temperature of about 200 °C, and three minutes allowed for temperature equilibration. The effect of the probe was to decrease the skin temperature and thereby decrease its permeability. On the basis that probe contact decreases the external skin temperature of the steel by 5 to 10 °C, and therefore the average steel temperature by 2.5 to 5 °C, at 200 °C, the decrease in permeability is 5 to 10%, causing an underestimate of corrosion by this amount.
2. The probe attachments on the fractionator were prone to removal of flux by a wind of 10-40 km/hr to which the West side of the fractionator was particularly exposed. Laboratory simulations indicated a 5-25% loss of capture efficiency of the probes employed in these circumstances.
3. Probes were regularly inspected for defects and replaced as necessary. However, inevitably they were subject to a 0-5% decrease in capture efficiency arising from this effect.

In short then, the circumstances of probe exposure led to a decrease in measured flux of 10 to 44%, in addition to other causes of hydrogen flux ‘loss’ discussed above.

FLUX-CORROSION RATE CORRELATION

Combining (ix) with (xi) and (xii) we obtain,

$$C = 2.96 \cdot 10^{-6} J_{ss.w.} \exp(4125/T) \text{ pL} \cdot \text{cm}^{-1} \cdot \text{s}^{-1} \cdot \text{bar}^{-1/2} \quad (\text{xiv})$$

⁽²⁾ HT-R (high temperature roaming) flux probe, Ion Science Ltd

A graph enabling prediction of corrosion rate from flux x thickness using equation (xiv) is shown in Figure 3. The above narrative indicates that the predicted corrosion rate using the roaming field probe was probably correct to within a factor of two. A much improved correlation would be obtained with a larger fixed probe, under insulation, as skin temperature effects and 'wind stripping', and positional variability would then be eliminated.

FIELD CORRELATION RESULTS

Test points for routine flux measurement were demarcated on the visbreaker fractionator at or near the locations of high corrosivity, from which insulation had been stripped. The measurement sites were either located on the West or East side of the fractionator as discussed in a contemporary paper. Those on the West side were exposed to moisture laden wind. On each side, about ten sites were identified as subject to high, and about six subject to low, corrosion. Flux measurements at some sites became redundant as repairs were made to the interior. Measurements were carried at each site some three times a week over a period of 49 days to 30 January.

The entire time sequenced results for sites subject to high corrosion on the East and West sides of the fractionator are presented in Figures 4 and 5 respectively. In both cases, flux at sites co-trend reasonably well. That is, a site was liable to show relatively high or low flux as compared to other sites, irrespective of the average flux on any given occasion. This is to be expected, since the variation in corrosivity, and therefore possibly flux, was defined by foregoing process conditions, whereas site dependent differences in flux would be expected from the influence of internal geometry on that shear velocity².

However, flux at the East were some 10 times higher than on the West side, despite the average corrosion rates on the two sides, over a period of 222 days to 10 Jan 2009, being 6.1 and 5.9 mm/yr respectively. There may have been several contributory factors at work here. Firstly, the East side measurements were carried out at a level some 4 trays down from the West side. It is possible that during the flux measurement epoch a temperature difference between the two was several 10's °C lower on the West side, increasing its permeability according to equation (xi) by a factor of 1.7. More fundamentally, the temperature drop would profoundly influence corrosion. Moreover, as mentioned above, prevailing weather and spray impacting the West side of the fractionator was expected to cool the skin temperature of the West side as compared to the East, as well as decreasing measured flux.

In Figure 6 the corrosion rates predicted from flux measurements on the East side are plotted against the UT derived corrosion rates. As can be seen, the correlation is extremely good, although it is appreciated that given the short time over which flux is averaged, good correlation is not fully proven by the results.

CONCLUSIONS

A laboratory based correlation between hydrogen flux measurements and naphthenic acid corrosion rates was developed on the basis that flux is determined by the hydrogen activity at a corroding surface, and this activity is proportional to corrosion rate. Errors associated with assumptions implicit to the correlation were evaluated. In its use on a visbreaker fractionator, known to be sustaining high corrosion rates over an 8 month interval, and using a 60 mm hydrogen efflux probe highly exposed to windy conditions, the correlation was expected to predict corrosion rates correct to within a factor of two.

A 50 day spot flux monitoring regime at about 40 sites showed approximate co-trending of flux at various sites, indicative that only two or three sites of high flux could be used to monitor an entire high temperature corrosion induced flux scenario. Flux at sites of low corrosivity delivered throughout the measurement period distinctly lower flux.

Flux on the side of the fractionator exposed to prevailing wind and spray were some 10 times lower than on the lea side. This could be attributable to the difference in corrosivity at the sites during the flux measurement campaign, in addition to the lea side being at a higher process temperature, being less cooled by prevailing winds, and being less subject to 'wind stripping' of measured flux to which the roaming probe used in the campaign was subject.

In general the flux measurements were useful in highlighting a severe corrosion episode and discerning changes in corrosivity caused by corrosion control of the corrosion. Improved insights might be gleaned from continuous monitoring of fewer sites, and flux monitored under insulation to avoid the deleterious effects of wind on flux measurement and corrosion correlation.

FIGURES

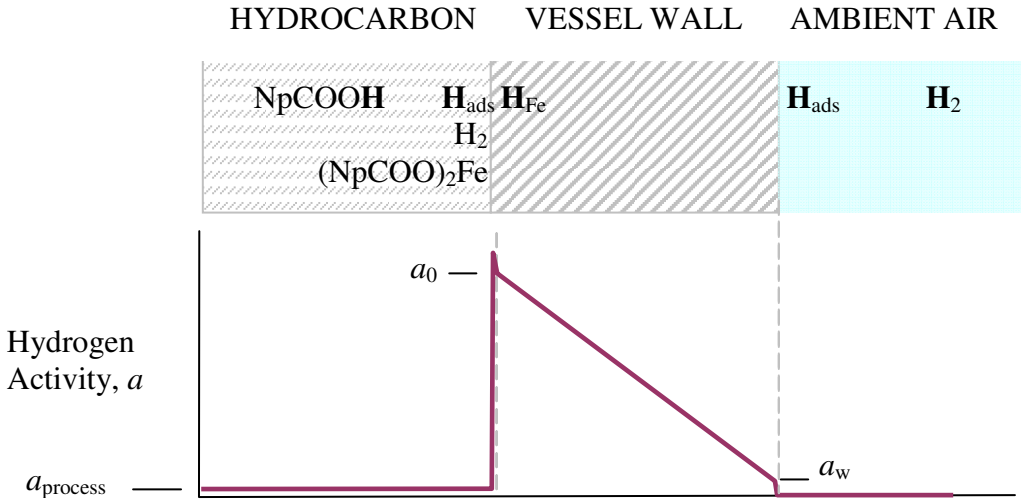


FIGURE 1. Schematic illustration of high temperature corrosion (NAC) induced hydrogen permeation, as discussed in the text.

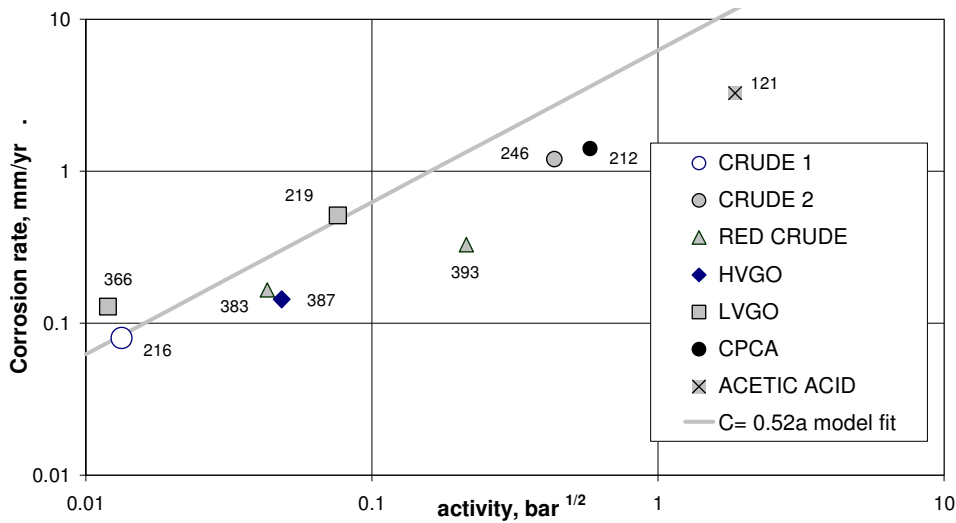


FIGURE 2. Correlation of corrosion rate and a_0 deduced from laboratory experiments with various corrosive liqueurs under reflux as detailed elsewhere⁷. Numbers refer to maximum temperature. Mild steel of $w = 0.2$ cm was tested. The correlation used in this work is shown by the line.

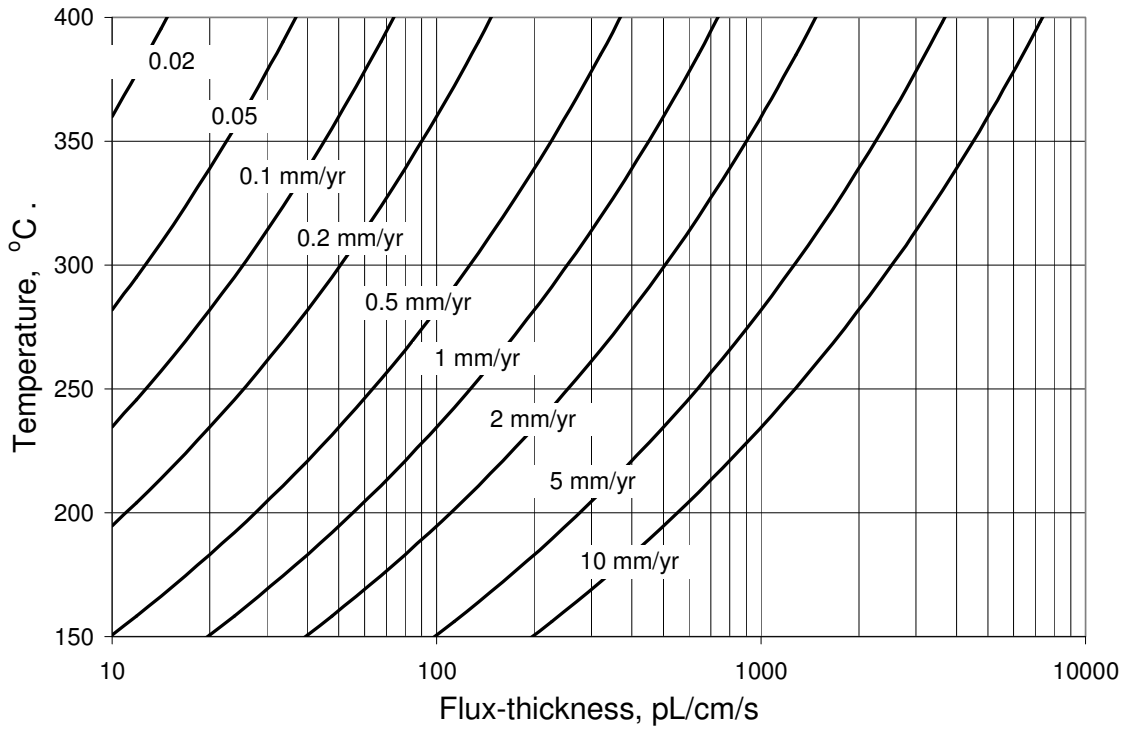


FIGURE 3. Chart for estimating corrosion rates from flux-thickness between 150 and 400 °C, for mild steel⁽³⁾. For example, a flux of 500 pL/cm²/s through 1 cm steel at 300 °C is indicative of a corrosion rate of 2 mm/yr. The correlation should be used with cautiously until further field data is obtained.

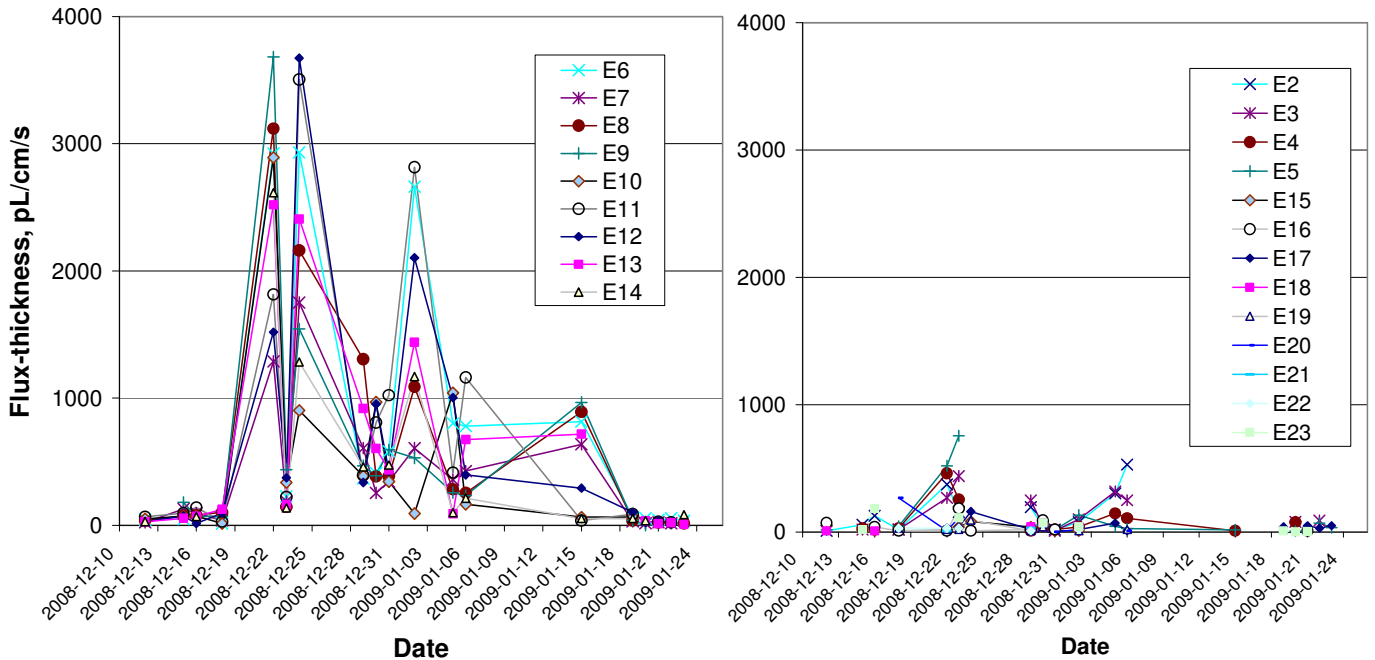


FIGURE 4. East side flux x thickness profiles during entire 50 day flux measurement campaign. The left-hand graph shows measurements on sites at which wall losses over an overlapping 8 month period exceeded 2 mm/yr, averaging 6.2 mm/yr, and the right-hand graph sites where corrosion was less than 2 mm/yr, averaging 0.6 mm/yr.

⁽³⁾ Flux-thickness is obtained by multiplying the steel thickness measured in cm by the flux, measured in pL/cm²/s, where 1 pL is 10⁻⁹ L hydrogen at 1 bar and 20 °C.

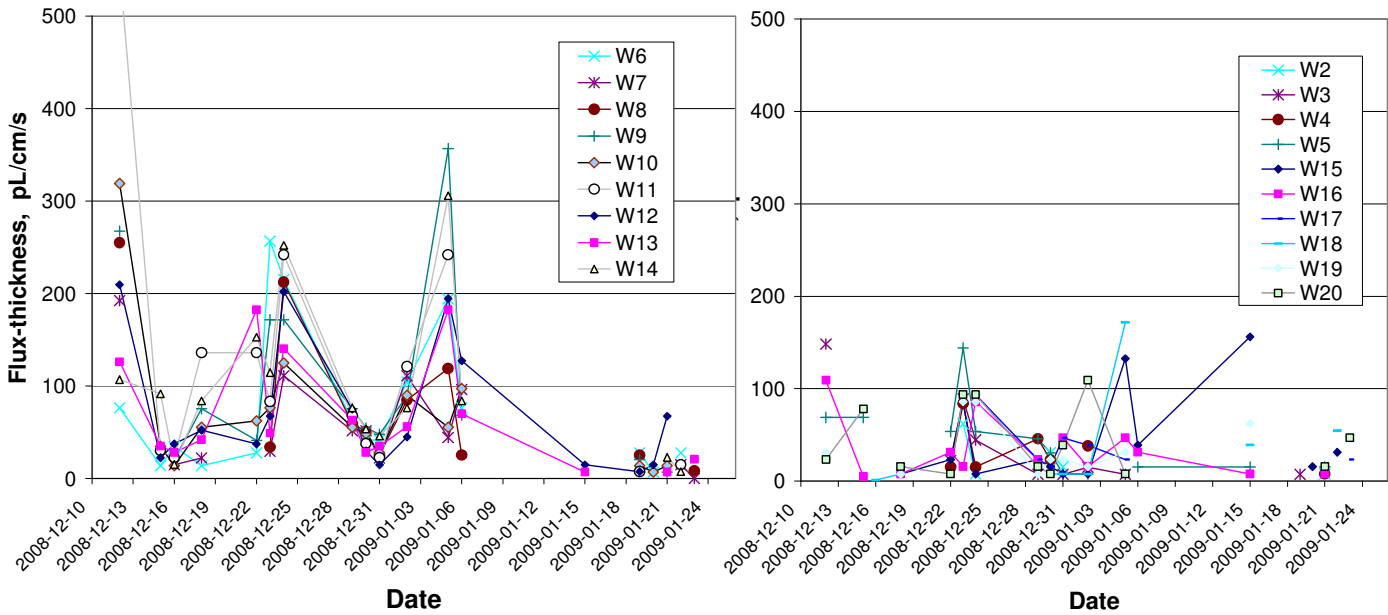


FIGURE 5. Westside of fractionator flux x thickness profiles during entire 50 day flux measurement epoch. The left had graph shows measurements on sites at which wall losses over an overlapping 8 months had exceeded 2 mm/yr, averaging 5.9 mm/yr, and the right hand graph sites where corrosion was less than 2 mm/yr, averaging 0.5 mm/yr.

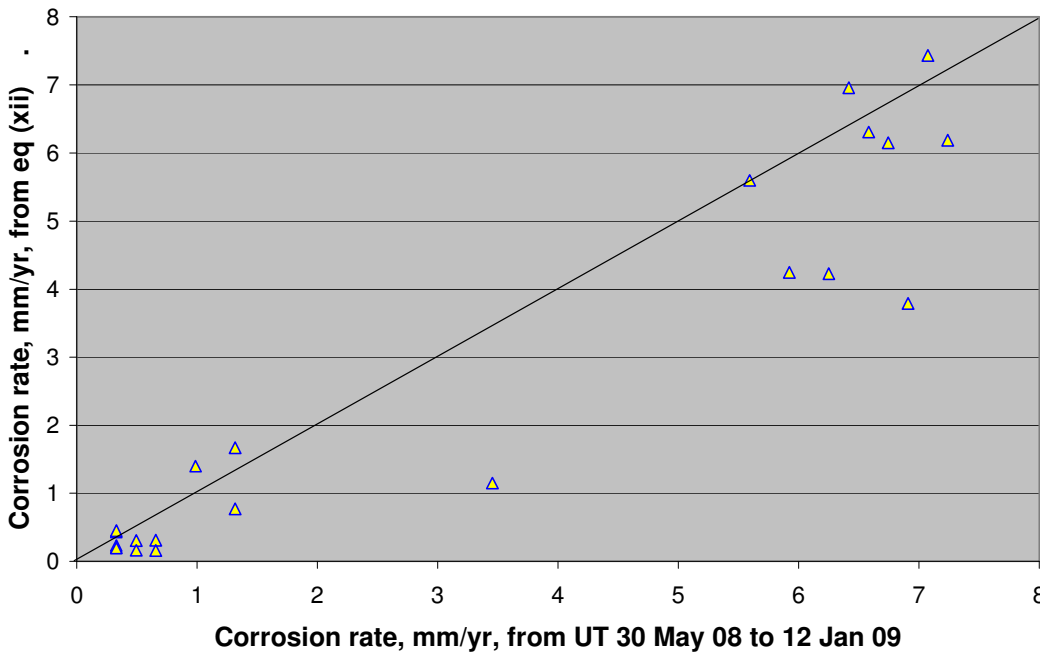


FIGURE 6. East side of fractionator flux profiles during entire 50 day measurement epoch versus corrosion rates calculated from UT measurements spanning an 8 month overlapping period. The equivalent graph for the West side is not complete due to overcladding, but also generally the correlation is poorer for reasons discussed in the text.

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