

DETECTION AND MONITORING OF NAPHTHENIC ACID CORROSION IN A VISBREAKER UNIT USING HYDROGEN FLUX MEASUREMENTS

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ABSTRACT

Corrosion rates of up to 0.8 mm/per month were detected on a Visbreaker fractionation column. Internal examination of the column showed that the shell corrosion was confined to the vicinity of four trays situated approximately two thirds of the way up the column, with the highest rates being seen within the downcomers. Examination of the corroded areas within the downcomers indicated the presence of smooth, uniform zones of metal loss characteristic of organic acid corrosion. Further analyses of both the internal deposits and sections of shell plate taken from the areas of high corrosion indicated that organic acids were present. While the column was on-line, hydrogen flux measurements were recorded in the areas of active corrosion in order to provide an estimate of the corrosion rate in real time, to monitor the extent of active corrosion, to determine the probable cause of corrosion and to assess the effectiveness of a newly-initiated corrosion inhibitor program. The corrosion rate estimations were found to correlate well with ultrasonic thickness measurements. Hydrogen flux measurements also confirmed that the injection of a filming amine inhibitor was effective in reducing the corrosion rate of the affected area by 10-fold, despite the high temperature of up to 220°C

Keywords: Naphthenic Acid, Visbreaker, Hydrogen Flux, Corrosion Inhibitor, TAN, Soaker Severity, High-Severity

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INTRODUCTION

Naphthenic acid corrosion (NAC) commonly occurs in refinery streams operating between 218-400°C, and most typically affects crude and vacuum units¹. The corrosion rate on carbon and low alloy steels is a function of the Total Acid Number (TAN), sulfur content, temperature, and fluid flow conditions. Mo additions to stainless steel produce alloys with useful resistance to NAC.

Corrosion at temperatures below 218°C has been reported in several circumstances:

- In atmospheric overhead systems, lighter organic acids (acetic, formic, etc.) present in the acidic crudes can cause corrosion.
- In vacuum overhead systems, light organic acids formed by the degradation of naphthenic acids in the vacuum feed furnace may be present and have also caused corrosion.
- In vacuum systems, corrosion at temperatures as low as 180°C has been reported due to true naphthenic acids^{13,14} although the true boiling point of these acids would be expected to be much higher.

Iron sulfide scale typically forms a semi-protective barrier against naphthenic acid attack. The scale can be removed by high wall shear stress (e.g. high velocity), which exposes the fresh metal beneath to further corrosion. Naphthenic acids can also convert iron sulfide to oil soluble iron naphthenate, which weakens and helps remove the scale. The presence of more active sulfur species (e.g. H_2S) tends to stabilize the sulfide scale against this latter form of attack. The net result of these effects is that naphthenic acid corrosion behavior can be time variant, localized, and difficult to predict.

The Visbreaker unit (VBU) discussed in this paper is a Shell Soaker type arrangement, manufactured in 1982. The unit is designed to upgrade bottoms products from the vacuum distillation unit to more valuable middle distillates by reducing the residue viscosity via thermal cracking. The fractionation tower is by SA516 grade 60 carbon steel, with an internal 410S SS cladding which terminates at tray 8. In the upper part of the column, trays 9-16 have carbon steel support rings, while the lower clad region has Type 405 SS rings. All trays are Type 410 stainless steel.

The use of hydrogen flux measurement to infer corrosion rates is comparatively new. It depends upon hydrogen permeation, whereby a proportion of nascent hydrogen generated by acid corrosion enters the internal, corroding surface of the steel. This hydrogen diffuses through the metal to the external wall, where it recombines and desorbs as molecular hydrogen gas. The hydrogen flow per unit surface area through and out of the material is termed the hydrogen flux J, (pL.cm⁻².s⁻¹). From a measured hydrogen flux, it is possible to infer the internal corrosion rate of the material as described later. Hydrogen permeation is a relatively rapid process. In thin-wall vessels at elevated temperatures, this method allows for near real-time monitoring of internal corrosion activity.

BACKGROUND

Units upstream of the Visbreaker unit described in this paper typically process a slate of crudes with a TAN in the HVGO stream of above 1. The TAN of the vacuum resid fed to the VBU is not typically measured, but is estimated to be above 0.5 based on the measured values of the HVGO stream and the known characteristics of the crude oils being processed. This TAN level is above the TAN of 0.5 which has been widely adopted by refiners as a 'rule of thumb' lower threshold at which NAC may occur in crude and vacuum distillation units².

More recent experiences, such as discussed by Nugent and Dobis⁵ suggest that even lower TAN levels may be sufficient to cause NAC, referring to Venezuelan crude slates with an average TAN of 0.24. Susceptible units and equipment often feature molybdenum containing alloy upgrades to steels such as 316L or 317L as a NAC preventative measure. Piehl⁷ demonstrated that an alloy required at least 2

wt% Mo in order to provide any resistance to NAC. This was further discussed by Craig,⁵ who demonstrated the effect of increasing molybdenum content on the corrosion-resistance of steels.

Literature searches carried out by the authors and by industry⁴ have not revealed any previously reported cases of NAC in a Visbreaker Unit other than that caused by lighter acids (degradation products) in the overhead system, nor were the unit manufacturers aware of any when contacted.

Description of Corrosion Observed

Corrosion of the Visbreaker fractionation column was initially brought to light in April 2008 when a small, localized fire occurred due to a pin-hole leak on the East side in a downcomer below tray 12 (tray 16 being the uppermost). Smooth, uniform corrosion in highly localized areas was found within the downcomers from trays 10 to 14. Corrosion losses of up to 10.5 mm were also apparent at the circumference of the carbon steel support rings adjacent to the shell at tray 8 (see Figure 1) and at trays 10 to 14. Lesser levels of corrosion were seen in trays 9, 15 and 16. The corrosion was localized to areas of liquid flow, with a pattern that suggested it was related to fluid flow conditions.

The internal layout of the upper portion of the column and the corrosion in this area is detailed in Figure 2. The operating temperature at trays 10-14 where the corrosion was most severe ranged from about 180 to 220°C (~200°C at the perforation at tray 12). Also, the East side of the column was more corroded than the West side (see corrosion rates in Table 1).

Repairs and Corrosion Monitoring of the Column

Figure 3 details the repairs that were made during shutdowns in June 2008 and in February 2009. During the June 2008 shutdown, shell insert plates were installed near trays 12 and 13, and lap patches were installed in the area of trays 11 to 14. A tubular style carbon steel electric resistance probe was installed on the West side in the downcomer between trays 12/13, and a 5Cr probe was installed on the East side in the downcomer between trays 11/12.

In December 2008 nine months after the initial failure, a scheduled on-stream ultrasonic thickness monitoring (USTM) scan revealed corrosion rates of up to 0.8 mm/month (Table 1), so it was apparent that further repairs would be necessary. A filming amine was injected into the column via the top reflux starting in January 16th 2009 to minimize further metal loss. The repairs were performed in February 2009, including a monitored hydrogen bakeout prior to welding. Further external over-plates were installed over thinned areas of the shell, and 316L stainless steel 'splash plates' were fitted to the inside of the column in the downcomer area between trays 13 and 14 to try to prevent corrosive fluids impinging on the thinned shell sections.

To allow for enhanced on-stream monitoring, corrosion coupons were installed in place of the East side (5Cr) corrosion probe. Pressure gauges were installed in the new lap patches, to indicate if the vessel shell behind these areas corroded to failure. Additionally, a modification to the West side corrosion probe was made to allow for samples of the process fluid to be taken on-stream. The results of this corrosion monitoring program are described in a later section below.

IDENTIFICATION OF THE CORROSION MECHANISM

Sulfidation was quickly ruled out as a possible cause of corrosion due to the 180°C – 220°C temperature range, which is well below the 260°C temperature at which sulfidation is considered significant¹. Additionally, relatively low sulfur blends averaging 0.3 wt% in the whole crude had been processed, and both CS and 5Cr probes subsequently showed similar corrosion rates.

Amine-related salt corrosion was considered as a possible cause of corrosion, but was ruled out because the operating temperature of $180-230^{\circ}$ C in the corroding region between trays 8 - 14 is too high for amine chloride salts to form. Furthermore, no chlorides were found in the process fluids drawn from the West side probe fitting, and no amine salts were detected in the analysis of the corrosion product⁸ removed during internal inspection.

Consideration was also given to the potential for chloride salt sublimation due to either shock condensation from cooler returning liquid or from the potentially cooler temperature of the vessel walls. These were ruled out because they did not fit the observed corrosion profile. No significant corrosion was evident on the trays where cooler liquid was returned to the column through the gas oil pump around, nozzle 10 (Figure 2) at tray 10. Instead, corrosion of the tray supports and shell wall occurred over a span of 5-6 trays, rather than being localized between trays 9-11 as would have been expected from shock condensation. Likewise, sublimation on the vessel walls would have been more likely at the colder upper trays than the lower hotter ones, which again did not fit the observed corrosion pattern.

HCl corrosion was also dismissed, again due to the high operating temperature at the affected portion of the column rendering the presence of free water impossible.

It was noted that the operating temperatures at the corroded trays were within the lower end of the range at which NAC has been reported⁵. Additionally, the corrosivity of naphthenic acids was known to be strongly velocity-related^{4,5}. The visual appearance of the corroded areas was consistent with corrosion by organic acids. Specifically, the affected area had no adherent scale, had bright patches that appeared freshly corroded, had a pattern of surface roughness that suggested it was flow related. However, any naphthenic acids in the feed to the VBU would need to be degraded (cracked) to produce lighter acids in order to reach this upper portion of the column.

The same corrosion deposit sample analysis detected several organic acids, but primarily hexanoic acid ($C_5H_{11}COOH$). The boiling point of hexanoic acid (202°C) corresponds well with the temperature in the area of highest corrosion. Tray 12 operating at 200 °C was the most severely corroded of all the trays, with trays 10 -14 experiencing corrosion to a lesser degree.

Gas oil samples drawn at the tray 8 level from January 5 to January 21, 2009, were found to have TAN levels of 0.4 - 0.5. Analysis showed these to be primarily hexanoic and heptanoic acids, and lesser amounts of naphthenic acids (i.e. ring structures). Longer term trends of TAN levels were not available.

A recent report on the corrosivity of many light organic acids indicated a corrosion rate of about 2.5 and 4.5 mm/yr for hexanoic acid and heptanoic acids, respectively¹⁵.

In conclusion, it is believed that organic acid caused localized removal of the protective sulfide scale from the vessel, resulting in the accelerated metal loss that occurred. This conclusion is supported by:

- The lack of evidence of any competing corrosion mechanism operating within this area of the column (temperature too low for sulfidation and too high for chloride salts)
- Visual appearance of the corroded areas matching known organic acid corrosion
- Chemical analysis indicating the presence of corrosive organic acids such as hexanoic acid
- Operating conditions in the corroded area of the column being well within the range at which corrosion by organic acids is known to occur in other process units.

EFFECTS OF A HIGH-SEVERITY CAMPAIGN

During high severity operation, the soaker operating temperature, pressure and residence time is increased to increase the unit's yield. The increase in soaker pressure seen is attributable to the increase in temperature in the soaker drum and the resulting increased thermal cracking. Early data

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suggested that elevated hydrogen flux levels and increased corrosion rates coincided with periods of high severity, suggesting that they were linked.

Possible explanations for the link between corrosion and operating regime include:

- 1. Increased Unit Throughput: By increasing the unit throughput, fluid velocities throughout the column increase. As the mechanism is believed to be a velocity-related form of organic acid corrosion, this would therefore increase corrosion rates in susceptible areas.
- 2. Increase in Molecular Cracking: During higher severity operation the residence time of the process fluid in the soaker is increased, and the temperature is increased slightly. This causes more thermal cracking to occur, which could also lead to cracking of the longer-chain organic acids, generating 'new', shorter-chain acids with lower boiling points (such as hexanoic acids).
- 3. Changes in the Crude Slate: Over time, a general, long-term shift towards processing higher-TAN crudes may have contributed to the corrosion.
- 4. Imported Residual Bottoms Products: These are purchased on the spot market and fed into the vacuum column, bypassing the corrosion inhibition program present on the atmospheric column. It is conceivable that acids from these are carrying over to the Visbreaker and providing the acids necessary for organic acid corrosion to occur.

It is important to note that the increase in throughput (hence fluid flow velocity) and the creation of these acids would work in tandem to increase the corrosion rate.

ON-STREAM MONITORING OF CORROSION

During the course of the previously described events, on-stream corrosion monitoring had been performed that provided further insight into the corrosion rate, the likely mechanism, and the effectiveness of measures taken to control it.

In May 2008, USTM scans were performed over the top section of the column. This survey revealed internal thinning in the area above the tray support rings between trays 8 and 16, and the downcomer area between trays 10 and 14 on the East and West sides of the column, quantified in Table 1. Prior USTM scans had not been carried out in the exact areas of corrosion, so it was not possible to calculate a corrosion rate. A long-term corrosion monitoring program was implemented, to enable any future corrosion in this area to be detected.

After the USTM scans, the column was internally cleaned using a citrus based chemical agent to permit a full internal inspection in June 2008. During this internal inspection the areas of corrosion (as described earlier in this document) were noted, and the deposit samples were taken for analysis. It is true that the citrus could have removed chloride salt deposits that were previously discussed (and dismissed) as a possible cause of corrosion. However, it should also be noted that samples drawn via the corrosion probe fitting at tray 13 while the column was operating did not detect any chlorides.

To allow comprehensive USTM scans to be carried out, the insulation was not reinstated on the affected area. USTM grids were also drawn to enable accurate data comparison. After the initial scan on 10 May 2008, the fractionator was subsequently scanned on 30 May 2008 after repairs, on 17 November 2008 after significant continued corrosion was indicated by probes, and on 7 January 2009, towards the end of a regime of hydrogen flux measurements. Corrosive wall loss of up to 4.4 mm was noted in November.

It was decided to attempt to utilize hydrogen flux measurement technology ⁽¹⁾ as a way of measuring corrosion. Hydrogen flux readings were taken between 12 December 2008 and 23 January 2009, to provide a near real-time indicator of where and when corrosion was occurring. The flux readings were then sent to one of the authors (who was unaware of the USTM measurements), to calculate the corrosion rate indicated by the hydrogen flux. The results corresponded well with the USTM derived rate, as further discussed below. The application of the hydrogen flux measurement technology to this issue is discussed in more depth later on in this document, and in greater detail in another paper by the authors⁹. The flux measurement was also used as a way to monitor the effectiveness of a corrosion inhibitor that was injected into the column, as discussed later.

After the January 2009 UTSM scans detected the high rates of wall thickness loss, the column was shut down in February 2009 and cleaned internally for inspection and further repair. The corrosion was manifesting itself in the same areas as previously active, and had a similar appearance. Corrosion rates appeared to be higher on the East side of the column than the West, as shown in Table 1. A possible explanation is that there may be a temperature differential across the column due to the prevailing wind which typically blows from the West. This would have an even greater cooling effect on this portion of the column which remained uninsulated since the initial failure. This could also account for the lower hydrogen flux readings detected on the West side of the column as discussed below.

The February 2009 repairs included lap patches which made it impossible to continue measuring the hydrogen flux in the corroded areas, since there was now a void between the shell and the lap patch. Any atomic hydrogen permeating the shell would recombine in this void, rendering it impossible to detect at the outside (patch) surface. Pressure gauges were therefore installed into the lap patches to indicate when the vessel shell beneath them had corroded to failure.

Four months after injecting filming amine, a corrosion coupon was fitted in place of the 5 Cr probe. This was pulled 34 days later. The coupon exhibited a smooth, uniformly corroded surface, characteristic of organic acid corrosion, but with a corrosion rate of only 0.65 mm/yr. Prior to the injection of the filming amine, the corrosion rate had been about 10 mm/yr as measured by USTM and corroborated by hydrogen flux monitoring. The operating mode of the column had not changed during this time period. This provides strong evidence that the filmer was successfully inhibiting the corrosion and, by inference, provides further confidence that the corrosion was caused by organic acids. If amine chloride salts had been responsible for the corrosion, then it is considered unlikely that a filming amine would penetrate underneath them and inhibit the corrosion.

Quantifying Corrosion Rates via Hydrogen Flux Readings

Flux measurements were taken using a 60 mm 'High Temperature Roaming' probe on surface of the fractionator, at specific grid reference sites that were correlated to USTM monitoring locations. Readings were manually recorded. The details of data correlation are presented in a contemporaneous paper ⁹. The relationship between hydrogen activity and corrosion rate is as follows ^{9,10}

Corrosion rate (mm/yr) = 5.22 a_0

(1)

 a_0 (bar^{-1/2}) is the steel entry face activity given by:

¹ Hydrosteel 6000 and Hydrosteel HT-R roaming high temperature hydrogen flux measurement probe, Ion Science Ltd, UK

 $a_0 = J w/P$

(2)

(3)

where *J* is the steady state flux (pL/cm²/s), *w* (cm) the steel thickness and P (Ncm³.cm⁻¹.s⁻¹.bar^{-1/2}) is the permeability, and P, for carbon steel is given by [Grabke and Riecke, 2000]¹¹:

 $P = 0.00186 \exp(4126/T)$

T (K) is the wall temperature. Combined,

Corrosion rate (mm/yr) = 5.22 J w./[0.00186 exp(4126/T)] (4)

In Figure 4 all recorded flux data is presented for the West and East side of the fractionator. The collation of flux from different sites is reasonable, and though the East and West side data sets show broadly the same corrosion episode, there is some difference in detail. Moreover, the flux on the East side is about 10 times higher. This is believed to be due in part to asymmetry within the fractionator, and in part due to a cooling by moisture laden westerly winds from the cooling towers to the west, to which the uninsulated fractionator was very exposed.

Hydrogen permeation through steel is very temperature dependent. For a 200 °C process temperature, a 20 km/hr direct wind is expected to decrease the surface temperature by 20 °C, the average wall temperature by about 10 °C, and hydrogen permeability by about 17 % according to (3), whereby the corrosion rate may be underestimated by the same amount. A further decrease in flux of some 15-30% is expected from the 'stripping' of measured flux collected from sites on the exposed West side, as discussed in detail elsewhere⁹. In short, these factors, as well as an underlying decrease in corrosion on the West side of the fractionator caused by exposure to high winds, may all have contributed to the observed decrease in flux on the West side.

The estimated corrosion rates for each test site, derived from time weighted average flux-thickness data between the period December 12, 2008 and January 23, 2009, converted into corrosion rates according to equation (4), are presented in Figure 5, together with corrosion rates derived from UT data on 30 May 2008 and 7 January 2009. The agreement between the flux and UT thickness derived rates on the West side is remarkable, given that the time frames are so different. It might be concluded that corrosion had been very severe for the entire time frame of the UT measurements. It is also noticeable that high flux readings are exclusively registered at sites of high corrosion.

In Figure 6a and 6b, real time corrosion rates are estimated from average flux at all the sites of high corrosion, and plotted against various process variables, including whole crude S and whole crude TAN. There is no clear trending with any particular variable, except possibly one might say that the high flux excursions around 23 December 2008 coincided with a significant process upset, evinced by the variable temperature.

INHIBITION OF CORROSION

Due to the corrosion rates evident in the column, it was decided in January 2009 to inject a corrosion inhibitor into the column via the naphtha reflux stream at the top of the column. The corrosion inhibitor chosen was a filming amine, designed to form a tightly-adherent protective film on the internal surface of the metal. The purpose of the film is to protect the underlying metal surface from attack by the corrosive species.

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Previous literature¹² states that "*traditional filming amine corrosion inhibitors are ineffective in this application*", due to "*inadequate thermal stability and the absence of a sulfide scale which many filming amines require to be effective*". The contracting company responsible for chemical inhibition believed that their proprietary inhibitor did not suffer from these drawbacks, and represented the best available chemical for this application. Phosphorus-based inhibitors are more commonly used for the mitigation of naphthenic acid corrosion, however it was felt that in this application they would not be as effective as the amine-based inhibitor, primarily due to the higher temperatures required to activate them⁸, meaning they would not be operating at their full effectiveness in the area of the column where protection was required.

Due to the uncertainty of the effectiveness of the filmer, hydrogen flux measurements were used to verify that the inhibitor was performing as desired. The formation of generates nascent hydrogen by reaction (5), which can then enter and diffuse through the steel forming the vessel shell.

 $Fe + 2 \operatorname{RCOOH} \rightarrow \operatorname{Fe}(\operatorname{RCOO})_2 + 2 \operatorname{H}^{\circ}$ (5)

A significant decrease in levels of hydrogen flux detected on the exterior surface of the vessel would therefore provide an indication of inhibitor effectiveness.

Figure 6a shows the effect of introducing the filmer into the fractionator column on the measured hydrogen flux readings. The filmer was introduced on the 16th January, and was expected to take up to 48 hours to become active. By the time of the next hydrogen flux measurement (19th January), hydrogen flux readings on both sides showed a significant decrease from their previous levels, dropping by almost a factor of ten on the East Side of the column. These low readings continued until the cessation of monitoring on 23rd January.

Other process conditions that could have affected the hydrogen flux held constant over this period. Temperature has a large effect on the solubility and diffusivity of hydrogen in the steel¹⁰. Temperatures at tray 8 and at the soaker outlet remained roughly constant from the 29th December (well before the filmer injection date) through to the 25th January (well after the hydrogen flux readings had decreased to near zero). The relative constancy in temperature within the column over the period of intensive monitoring proves that the variation in hydrogen flux is not attributable to any short-term temperature variations in the column.

The feed rate to the column was monitored throughout this period, and was found to be increasing at the time the inhibitor was injected (see Figure 6b). Increased feed rate would increase the fluid flow and velocities within the column, and would tend to increase corrosion, so this can also be rejected as a possible explanation for any decrease in corrosion rate and hydrogen flux.

The TAN content of the crude was also monitored, to see if a decrease in TAN would account for lower levels of corrosion. From the 5th January until the 21st January, the TAN of the crude blend increased significantly, from 0.13 to a maximum of 0.53. TAN levels in the VBU gas oil draw increased only slightly during this period to near 0.5, while TAN of the naphtha draw increased several-fold to about 0.4. As levels of NAC (and thus quantities of hydrogen generated) would be expected to increase with increasing TAN, this can also be ruled out as a factor that could cause the observed levels of corrosion rate and hydrogen flux to decrease.

The final process variable that could affect the rate of corrosion is the level of sulfur in the crude blend. It is possible for sulfur to inhibit NAC – Craig⁵ discusses how sulfidation can act to inhibit NAC, by supplying a protective iron sulfide scale. Although the sulfur levels in the crude increased after the corrosion inhibitor was injected, they still remained well within the range that the unit had been

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operating in over the previous several months (see table 1). When this is considered alongside the fact that the temperatures within the corroded areas of this column were only about 200°C, it is not likely that sulfidation affected or negated any organic acid corrosion during the period of interest.

Following on from the reasoning above, it is clear that the injection of a filming amine-based corrosion inhibitor manifested a rapid, quantifiable effect in reducing corrosion within the column, visible through a rapid drop in observed levels of hydrogen flux.

CONCLUSIONS

- Organic acids formed by decomposition of naphthenic acids can cause significant metal loss in Visbreaker units
- Hydrogen flux measurement can be used to track the activity of Naphthenic Acid Corrosion at 200 $^\circ\text{C}$
- Filming amines appear to be effective at controlling this particular corrosion mechanism.
- Further work and long-term monitoring is necessary in order to increase our understanding of this issue of lower temperature organic acid corrosion, and to further verify the conclusions drawn in this document

REFERENCES

- 1. American Petroleum Institute, Recommended Practice 571 "Damage Mechanisms Affecting Fixed Equipment in the Refining Industry", December 2003.
- 2. Derungs, W.A., "Naphthenic Acid Corrosion An Old Enemy of the Petroleum Industry", *Corrosion*, **12** (1956), 41.
- 3. Craig, H. L., "Temperature and Velocity Effects in Naphthenic Acid Corrosion", CORROSION/96, Paper No. 603, (Houston, TX: NACE, 1996)
- 4. Babaian-Kibala, E., Nugent, M.J, "Naphthenic Acid Corrosion Literature Survey", CORROSION/99 Paper No. 378, (Houston, Texas: NACE, 1999)
- 5. Nugent, M.J, Dobis, J.D., "Experience with Naphthenic Acid Corrosion in Low TAN Crudes", CORROSION/98, Paper No. 577, (Houston, Texas: NACE, 1998)
- 6. Private communication from Metamet Consultants Ltd.
- 7. Piehl, R. L., "Naphthenic Acid Corrosion in Crude Distillation Units", CORROSION/87, Paper 196, (Houston, Texas: NACE, 1987)
- 8. Private communication from Nalco company Energy Services Division.
- 9. Rudd, T.F., O'Kane, J.M., Harrison, J.H., Dean, F.W.H., Powell, S.J., "Correlation of Hydrogen Flux and Corrosion Rate Measurements Carried Out During a Severe Episode of Corrosion-Erosion Attributable to Naphthenic Acid", CORROSION 2010, (Houston, TX: NACE, 2010; *to be published*)
- 10. Dean, F.W.H., Powell, S.J., "Hydrogen Flux and High Temperature Acid Corrosion", CORROSION 2006, Paper No. 06436 (Houston, TX: NACE, 2006)

- 11. Grabke, H.J., Riecke, E., "Adsorpsion and Diffusion of Hydrogen in Steels", *Materiali in Tehnologije*, **34** (2000), pp 331-342.
- 12. Zetlmeisl, M.J., "Naphthenic Acid Corrosion and its Control", CORROSION/96, Paper No. 218, (Houston, Texas: NACE, 1996)
- Groysman, A., Brodsky, N., Pener, J., Goldis, A., Savchenko, N., "Study of Corrosiveness of Acidic Crude Oil and It's Fractions", CORROSION 2005, Paper No. 05686 (Houston, TX: NACE, 2005).
- 14. Kapusta, S.D., Ooms, A., van den Berg, F., Smith, A., Fort, W.C., "Safe Processing of Acid Crudes", CORROSION 2004, Paper No. 04637 (Houston, TX: NACE, 2004).
- 15. Groysman, A., Brodsky, N., Pener, J., Shmulevich, D., "Low Temperature Naphthenic Acid Corrosion Study", Corrosion 2007, Paper No. 07569 (Houston, TX: NACE, 2007)

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TABLE 1 EXTENT OF MEASURED METAL LOSS WITHIN THE COLUMN

Tray Level	Maximum Support Ring Wall Loss (mm)		Maximum Downcomer area Wall Loss (mm)		Corrosion Rate (mm/month)	
	Loss	% of ring corroded	West	East	West	East
15-16	1	40	0	0	0	0
14-15	2	40	0	0	0	0
13-14	9	40	4	5	0.25	0.8
12-13	9	40	4	0	0.7	0
11-12	7	40	0	Perforated	0	0.8
10-11	7	50	7	0	0.3	0
9-10	6	40	0	5	0	0.5

Italicised text denotes areas repaired with insert plates in June 2008 **Bold text** denotes areas lap patched in February 2009



FIGURE 1: Tray 8 support ring corrosion

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FIGURE 3: Location of insert plates, over plates (lap patches), splash plates and corrosion probes fitted to the column.



FIGURE 4: All hydrogen flux site readings



FIGURE 5: Comparison corrosion rate derived from hydrogen flux (50 days to 30 Jan 2009) to corrosion rate determined by ultrasonic thickness measurements (222 days to 10Jan 2009)



FIGURE 6a: Corrosion rate versus TAN and S. Note that TAN remains approximately level throughout the period, but that corrosion rate drops when filming inhibitor is introduced



FIGURE 6b: Additional operating variables during the period of corrosion monitoring (compare corrosion rates in Figure 6a)