New Naphthenic Crudes – Risk Assessment and chemical treatment with an example from Repsol YPF, Mendoza, Argentina

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General Concerns for Processing Naphthenic Crudes

Naphthenic acids are present in some crude oils as natural constituents, resulting from the precursor molecules in the original biomass and reactions of degradation over passing centuries. Figure 1 shows a generic structure for naphthenic acids. (The acidic functional group is in the upper right of the molecule.)

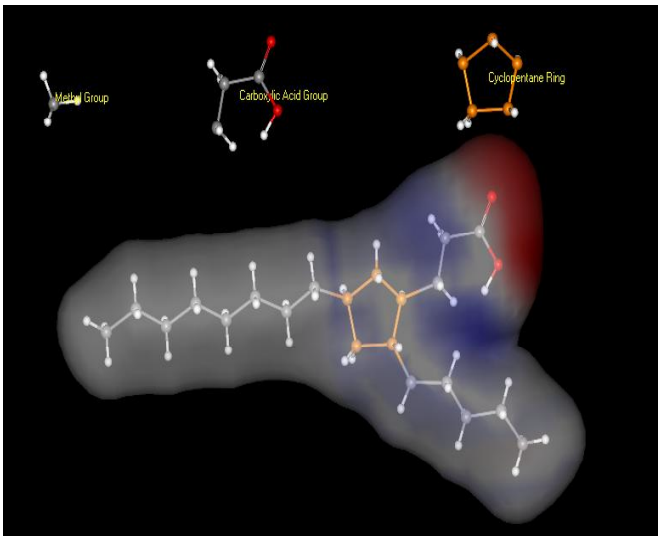


Figure 1 Generic Structure of Naphthenic Acids

The saturated ring part of the molecule is either five or six carbon atoms in size, and is responsible for the name "Naphthene". The carboxylic acid groups are responsible for the reactive behaviour with metals, whilst the alkyl substituents – especially the hydrocarbon group chains - are responsible for making the metal salts oil-soluble. The two properties are both important for the molecule's corrosion activity.

The quantity of acids present in a particular crude oil or distillate is usually measured as the Total Acid Number, or TAN. This titration includes all acids such as phenols and H2S, and a refinement of the method to separate out the naphthenic acids as a Naphthenic Acid Titration or NAT gives a more accurate picture of the potential for corrosion.

Naphthenic acids have a wide range of structures in any given crude or distillate, and the strength of the acids is partially dependent on the structure of the molecule. Acids with a sterically hindered carboxylic group will be weaker than those with a more open structure. The corrosivity of the molecules thus depends on the particular steric arrangement of the acid group(s) and side chains present, as well as the quantity of acids that are measured by a TAN or NAT titration

The oil-solubility of the metal naphthenates is responsible for the easy removal of the corrosion by-products from the reaction sites, leaving a freshly exposed surface where further attack can occur. The rate at which these soluble metal salts are removed from the substrates is accelerated by high liquid scouring rates of the surfaces, so the corrosion is more severe with high velocity liquid streams and in impingement zones. The hydrocarbon chain plays a strong part in the oil solubility of the molecules. In very light acids, where the alkyl group is short, the metal naphthenate salts will dissolve in the hydrocarbon fluids less readily than those formed with heavier acid molecules.

The molecular naphthenic acid structures dictate that the acids are not fractionated into the lighter distillates, so that corrosion problems should be restricted to the feed and residue streams, together with distillates boiling above about 200-220 °C NBP. The kerosene and lighter fractions should therefore not exhibit much naphthenic acid attack, although they may contain fragments of the naphthenic acids that have broken down under the thermal stresses in the furnaces.

The most common effect from breakdown fragments is to produce significant quantities of formic, acetic, and propionic acids in the overhead water condensates of both atmospheric and vacuum columns. These are often high enough to cause concern and increased neutralizing amine rates are required to control the aqueous strong acid corrosion. It is necessary to monitor for corrosion from these light acids in all distillation overhead systems, even in vacuum units where an extensive past history may have never detected corrosion damage.

In practice, the naphthenic acids concentrate into the heavier atmospheric gas oils and residue, as well as into the vacuum distillates and residue. Each naphthenic crude oil has its own pattern of acid distribution throughout the distillation temperature profile, and in some cases, a particular distillate stream may contain more than twice the acid concentration found in the raw crude. The chart below in figure 2 shows how the naphthenic acid fractions in a acid crude will concentrate differently for different crudes. The examples in the chart were chosen to illustrate the variability of the acid distribution in four common North Sea naphthenic crudes.

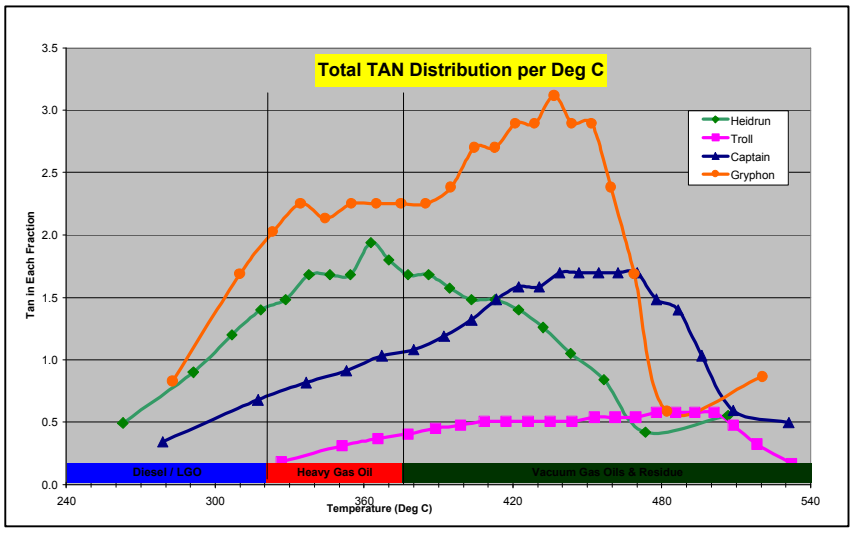


Figure 2 Naphthenic Concentration Profiles for Four North Sea Crude

It is clear that the Heidrun acids will tend to concentrate in the atmospheric column lower section and vacuum upper section, whereas Gryphon, Captain, and Troll acids will be concentrated more in the heavier vacuum distillates and residue. Other crudes will have their individual characteristic concentration patterns.

The naphthenic acids are readily destroyed in catalytic conversion units such as hydrotreaters and catalytic crackers. In hydrotreaters, the acids are converted to neutral alcohols, whilst in FCC reactors they are converted into CO_2 and the light organic acids mentioned previously. Thermal conversion units such as thermal crackers and visbreakers also degrade the naphthenic acids into lighter organic acids, which are recovered in the overhead condensates of their fractionators. Therefore, the treated hydrocarbon distillates from these units do not pose a threat from naphthenic acid attack. However, the overhead systems of the fractionators will require closer attention than in normal crude processing.

The same considerations apply to upstream fractionation towers, where an observed dramatic increase in light organic acid fragments has been known to corrode an untreated vacuum overhead condenser in less than six months. Likewise the atmospheric distillation overhead circuit may suffer when condensates from downstream plants are recycled as desalter wash water. The organic acids can partition into the crude during desalting, particularly if the water equilibrium pH (i.e. the effluent pH) from the desalter is acidic.

Nalco has a proprietary test method to measure the naphthenic acid content (NAT) of a stream. This has enabled us to build a database of crude properties where the naphthenic acid distribution is measured for various fractionation ranges. Curves similar to the TBP yield profile are constructed to show the naphthenic acid distributions against fractionation temperature. This database has both single crude data, and some blends from actual refinery feeds. However, the research effort to support this activity is such that not all the currently available naphthenic crudes have been characterized. We have not attempted to include actual molecular structures of the various acids present, as there are hundreds of possible oligamers for a given fraction. A precise structural knowledge of all the acids present would be of doubtful benefit in combating or predicting the practical effects of naphthenic corrosion.

The use of NAT or even TAN data only shows the quantity of the acids present. It does not indicate how corrosive those acids may be in a given environment. Nor does this data allow for the natural inhibition effects that arise from the reactive sulfur components in a crude blend. One of Nalco's multinational customers has built a proprietary software model to predict crude and distillate corrosivity, using the combined effects of naphthenic acid titration (NAT) and sulfur compounds. This relationship is also a subject of a current Joint Industry Project (JIP).

This approach is somewhat better than relying solely upon the NAT to anticipate where the most corrosion activity should be expected, but still needs to take into account the temperature, phase behavior, and localized shear effects for a total environment evaluation. The risk evaluation matrix then incorporates all these factors, together with plant metallurgy and remaining thickness measurements, before any estimation can be made for retirement predictions.

A more practical approach for a refinery that wishes to control corrosion with naphthenic crudes is to increase the number of sites of on-line corrosion monitoring. The addition of access stubs for injecting a chemical inhibitor with an injection quill, and for inserting corrosion probes, should be planned into the next scheduled shutdown. The existing inspection methods in many refineries have been adapted to a risk-based assessment for frequency and location of inspection. This has allowed a more focused approach to make better use of limited resources in manpower and equipment. When the previous history reflects the mechanisms that were dominant in high temperature corrosion from sulfidic attack, there will need to be a re-appraisal of the new phenomena that are introduced by naphthenic corrosion. In particular, the general metal loss that accompanies high temperature sulfidic attack will be modified to a localized pitting mechanism with naphthenic acids present. The wall penetration rate from this pitting attack can be up to ten times faster than the thickness loss from sulfidic attack.

This change in mode and location of corrosion creates uncertainty in the previously predicted retirement calculations. Because of this change, there need to be more frequent inspections, on a wider range of locations, than in the past. The change in mode, from a general corrosion mechanism to a localized pitting attack, requires that alternative measurement techniques be employed for detection.

The possible localization and rapid penetration rate that results from naphthenic acid corrosion means that there may not be adequate time to detect this corrosion onset by visual inspections at turnarounds. It should therefore be expected to occur, and inspection procedures increased accordingly. One of the prime areas of focus should be to undertake a full PMI (Positive Material Identification) program for all of the accessible pipework and mechanical containment vessels whilst the plant is running. This data is far from complete at most refineries, and any weak sections of a plant's metallurgy should be identified as soon as possible and inspected more frequently than usual.

CONTROLLING NAPHTHENIC ACID CORROSION

There are currently three options to manage corrosion effects from naphthenic acids in crude oils. Two of these – blending and metallurgy selection – have been available for many years. The third option – use of a chemical passivation program – has only been feasible within the last fifteen years.

Blending to an Acidity Limit

The corrosion of refinery units from naphthenic acid attack has traditionally been managed by processing only minor percentages of these crudes as components of the feed blend. Many refiners have adopted a limit on the TAN of the feed and product streams as an effective strategy for keeping the corrosion within acceptable rates. For example, in some cases the feed TAN has been kept below 0.3 mg/g KOH, whilst distillate streams have been allowed to have acidities up to 0.7 mg/g KOH.

Whilst this blending strategy has been widely practiced, with generally good results, the percentage of naphthenic crude that may be used in the feed blend has been low. The current marketing of new naphthenic crudes brings a significant discount relative to non-acidic crudes, and so the pressure on refineries to process higher percentages in their feed blends has increased.

Metallurgy Choice

The obvious means to process higher acidity crudes in greater percentages is to employ materials in construction of the refinery that are resistant to the mode of attack posed by naphthenic acids. This strategy is successfully employed to resist high-temperature sulfidation attack, by incorporating alloys with increased chromium content. Unfortunately, these alloys have very little extra

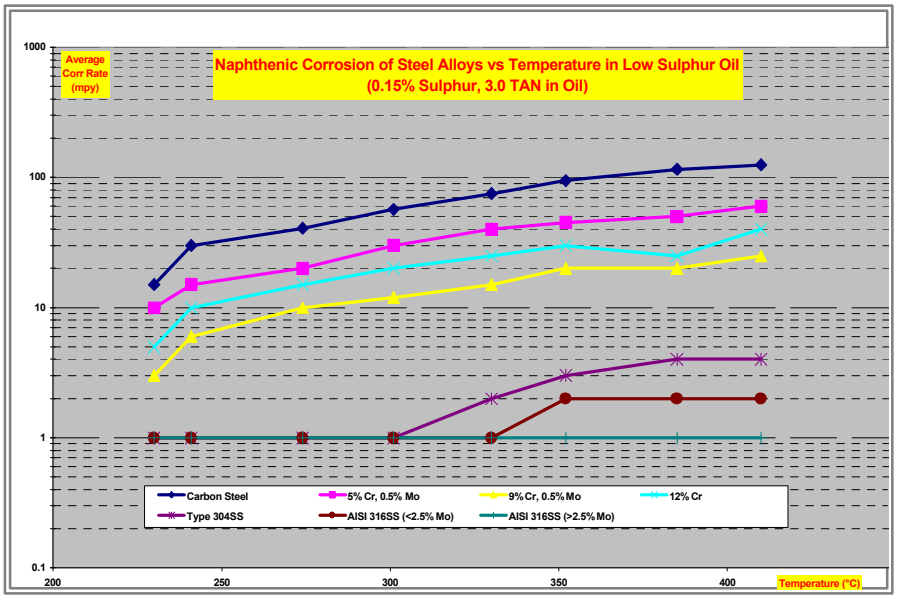


Figure 3: Metallurgical Resistance to Naphthenic Acids in Low Sulfur

resistance above that of carbon steel when exposed to naphthenic acid attack.

In Figures 3 and 4, the resistances of various common materials of construction (average corrosion rate from metal loss) from the refinery environment are plotted against acidity level.

For metallurgical protection against naphthenic acid attack, it is necessary to incorporate higher molybdenum into the alloy compositions. Several alloy grades are now available that have high molybdenum contents, notably the Ni-Mo Hastelloy grades.

The actual resistance to the overall corrosion mechanism (from both sulfur compounds and naphthenic acids) is also important.

From figure three it can be seen that in low sulfur oils the higher chromium levels do bring some protection, but not enough to be totally resistant. The austenitic stainless steels bring even greater resistance, but only 316SS has adequate resistance and even then, it should have more than 2.5% molybdenum (spec 2%-3% Mo) for the highest level of protection.

Of the materials commonly found in refinery and petrochemical environments, only AISI 316SS and AISI 317SS in the austenitic stainless steel family possess adequate resistance to naphthenic acid attack. The usual molybdenum specification for the two alloys is for 2.0-3.0% in 316SS and 3.0-4.0% in 317SS. However, there is a high Mo version of 316SS that has 2.5-3.0% Mo.

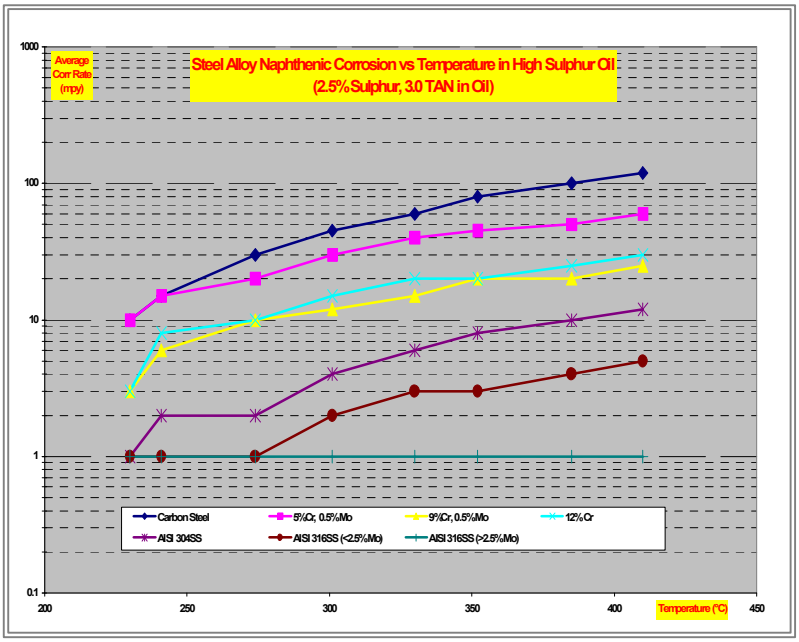


Figure 4: Metallurgical Resistance to Naphthenic Acids in High Sulfur Oils

By specifying all components in AISI 316SS to be above 2.5% molybdenum in any future purchases, there will be a significantly enhanced lifetime performance over the minimum grade 2% Mo alloy.

For existing refineries, built without the enhanced alloy materials above, the option to fully upgrade the metallurgy is too expensive and requires an extended shutdown period to upgrade the plant. However, there are minor upgrades possible where this will be by far the best solution. Such upgrades include the packing material for any structured mesh packing in fractionating column beds, and any zones where it may be impossible to use chemical passivation measures reliably. It may also be a preferred choice where certain components that could in future operate under severe threat from naphthenic acid attack, are already due for replacement.

In Figure 5 alongside, the benefits of small amounts of sulfur compounds in establishing a renewable protective film on plain carbon steel can be clearly seen.

However, as the sulfur content of the oil increases, the high-temperature sulfur corrosion attack becomes dominant.

The onset temperature and magnitude of this effect will vary depending on the specific sulfur compounds present.

Metallurgical Aspects

The minimum specification for ferrous alloys to possess worthwhile resistance to naphthenic acid corrosion is to incorporate at least 2.5% Molybdenum into the formulation. In one Venezuelan refinery, they carried out selective metallurgical upgrades that have enabled them to process local naphthenic crudes such as Tijuana Light successfully for over thirty-five years, in a time when chemical inhibitors were not available.

Of the common materials used in refining and petrochemical plant construction, some of the 300 series austenitic stainless steels fall within this category. AISI 316 specification calls for 2.0% to 3.0% Mo, so that the higher end of the specification for this alloy is acceptable. Not all batches of AISI 316SS fall into this category, so any purchase of AISI 316SS must include specific requirements for the Molybdenum content of the material. Better still is AISI 317, which specifies 3.0 to 4.0% molybdenum so that all grades of AISI 317SS are useful.

Other alloys with known naphthenic acid resistance are the nickel-based Hastelloy grades, which often contain more than 10% Mo. Hastelloy C-276 contains 17% Mo, whilst Hastelloy C-2000 contains 16% Mo. Other alloys proposed for resistance to naphthenic acids include Avesta 904L austenitic stainless steel (4-5 % Mo), and Al-6-XN (6-7 % Mo).

Where a plant does not possess adequate metallurgy to resist naphthenic acid corrosion, chemical inhibitors may be used to protect the more common steel grades such as carbon steel, low chrome alloys, and stainless steels with insufficient molybdenum content.

The protection philosophy for application of naphthenic corrosion inhibitors is based on passivation of susceptible metal surfaces. This is achieved by converting the ferrous alloy surfaces from a typical sulfide film into a complex poly-phosphate / thiophosphate layer, which is far more resistant to attack from naphthenic acids.

The predominate inhibitor chemistry that is used to generate the phosphate complex layers is an organic phosphate ester compound that becomes activated at elevated temperatures. The initiation of this activation step occurs at around 170-200 °C, and above this temperature, the concentrated chemicals are aggressive to all common alloys and materials used in refinery construction.

CORROSION MONITORING & INSPECTION

The monitoring of corrosion is a crucial factor in successfully processing naphthenic crudes. Far more inspections are required and extra monitoring equipment must be installed. It is important that this step is taken before naphthenic feeds are increased, so that the underlying corrosion rates from sulfidic attack can be established ahead of the increased corrosivity regime that accompanies naphthenic crude processing.

The inspection routines that have become established in recent years for targeting the areas of increased risk must be re-examined when naphthenic crudes are introduced. The historical modes of corrosion in high temperature areas have mostly been sulfidic in nature, and the type of damage caused with this mechanism is a general attack. Naphthenic acid corrosion is a pitting mechanism, or in extreme cases, deep gouging of the metal and it can be very localized.

The localized nature of naphthenic corrosion means that far more measurements are required from techniques such as ultrasonic thickness or X-Ray surveys, but it also means that their chances of successful detection of the attack can be diminished. There are other factors, such as the widespread use of thermal insulation on these high temperature pipes, and often the remoteness of the pipes from easy reach from normal platforms, that make such inspections more costly and time-consuming.

The change in mechanism to a pitting attack can also result in far quicker perforation of the metal than previously expected from sulfidation, and this necessitates that corrosion measurement techniques be used that have quicker response times. They also have to work in a difficult thermal environment, and normal corrosion probes are unsuitable in standard form.

The newer techniques that have been developed to help in the monitoring of naphthenic corrosion include ii-Corr's Field Signature Method (FSM) and Ion Science's Hydrosteel 6000 Probe (where a sulfidic component is present). There are also ultra-sensitive ultrasonic thickness measurement devices coming into the Industry.

Extensions of the traditional electrical resistance probe (ER) technology have been available for many years in specialized high temperature versions, and a more recent development from Cormon with their CEION® probes has produced much faster response times and / or longer probe lifetimes.

The authors recommend that all of these methods be considered for implementation in refineries that increase the acidity of the feed to any significant extent.

Corrosion Monitoring Locations

Monitoring focuses on streams and materials that are susceptible to attack. Specific recommendations for monitoring locations and techniques have been presented in a previous section. When using the tables, it is useful to gain an overall perspective by considering three regimes of naphthenic acid corrosion:

- High velocity (usually over 30 meters/second) two-phase flow: This is primarily found in places such as the last few tubes of atmospheric and vacuum furnaces, the furnace transfer lines, and the immediate flash zones of columns. This is a severe service corrosion monitoring is difficult, and, if not done carefully, monitoring probes can actually increase corrosion by inducing turbulence.

- Condensing acid vapors: This is often found in columns, particularly in vacuum columns and packing down to temperatures of 177°C. Corrosion often takes the form of "rivulets" as the acid runs down and gouges out the material.

- Moderate velocity erosion/corrosion. There is no well-defined lower velocity for this corrosion and it is very sensitive to turbulence (shear stress) at such locations as control valves, elbows, orifice plates, and pumps. At the same velocities, smaller diameter piping will tend to show more erosion/corrosion than larger piping due to wall shear stress effects. These conditions are most often in side cut piping, but can be in bottoms piping. This zone is also sensitive to sulfidation effects. Depending on the exact nature of sulfide scales formed with the particular crude, the presence of sulfur compounds can increase corrosion, but can also significantly inhibit corrosion. The corrosion monitoring locations given in the figures and tables attempt to monitor all three regimes.

Choice of Monitoring Techniques

No single monitoring method should be used alone. Possible techniques include electrical resistance probes, corrosion coupons, field signature method monitoring, stream sampling for analysis, and conventional equipment inspection techniques.

Baseline corrosion monitoring should be performed before the high acid crude is run. We recommend accumulating a minimum of 30-60 days of baseline data at each blending increment, until the final blending target is achieved. Monitor and note any correlation of the corrosion rates with crude slate changes, or other significant process changes.

Electric Resistance (ER) Probes

Early Electric Resistance probes simply used a wire of the same material as the pipe or equipment of interest, and measured the change in resistance as the wire corroded. As the wire corrodes it becomes thinner, the resistance increases, and the change in resistance with time can be correlated to corrosion rate in mils per year, mpy. Today we more often use a tubular ER probe or a flush mounted probe that has elements within the probe such that it does not protrude through the wall, but the concept is the same.

ER probes are simple, reliable, and inexpensive. They can have problems with sensitivity and temperature fluctuations (discussed below), pitting (hence the reason we typically use tubular or flush mounted style today), and iron sulfide scales interfering with the readings. In choosing traditional probes, one must sacrifice sensitivity versus longevity of the probe, which can be a problem if the probe

cannot be readily retracted and replaced. The newer "CEION®" probes discussed below largely overcome these limitations. But still, the traditional ER probes overall do a good job of assessing long term corrosion trends and detecting major corrosion changes over a few days or weeks. The retractable style of probes can also be fitted with corrosion coupons on the end.

Electric Resistance probes need to be specified as "high temperature capable," which essentially means that the housing and sealing system are capable of withstanding higher temperature exposure. This means that the element will be seal welded to the mounting device for the highest reliability. In flush mounted probes, the seal welding is not possible and a ceramic sealing device is often employed. The ceramic seals have proven troublesome in their high temperature sealing capability. The retractable probes require a minimum 1½" valve with a full port. The metallic element should be specified as the same metallurgy as the surrounding equipment (i.e., CS, 5Cr, 9Cr, etc.).

The primary problem associated with ER Probes is a lack of sensitivity and the fluctuation of data due to inadequate temperature compensation. The probe must be inserted deep enough into the line, so that the reference probe remains at the stream temperature. The probe must also be adequately insulated. For high temperature, monitoring, statistical compensation is recommended, by increasing the number of data points in comparison to low temperature monitoring. We would recommend measurements in 3-hour intervals, until the reading stabilizes and is believable.

CAUTION: Use of tubular ER probes or coupons on a transfer line is not recommeneded. The high velocity of these multiphase lines may cause severe, hard-to-detect, local corrosion and failure. Flush mounted ER probes could be employed in these high velocity locations, as they cause less turbulence. (Note that flush-mount probes are more prone to fluctuations, caused by a larger temperature gradient with the reference probe.)

THICKNESS MONITORING AND RADIOGRAPHY

Piping systems are generally subject to higher corrosion rates at points of natural turbulence. Piping just downstream of control valves, thermowells, and orifice plates is particularly suspect. Elbows and piping just downstream of the circumferential weld of the fitting are also susceptible.

Establish a complete baseline measurement database for the line numbers that are identified for corrosion monitoring. The current level of inspection, which has been performed to date, will need to be increased to include all of the most critical locations (i.e. elbows, tees, branch connections, reducers, orifice plates, pump discharge piping, pressure and flow control stations). One of the critical areas to be considered will be the downstream block valve on modulating control valve stations.

The proposed method of inspection is either ultrasonic thickness measurement or profile radiography. New digital radiographic techniques are superior to the film only type as this technique gives a reading of the thickness directly. The Refinery Inspection Group will determine the most effective inspection method based on their experience. Additionally, isometrics need to be produced identifying clearly the line numbers using accurate dimensional scale, which should reflect the extent of inspection. The baseline must be completed before introduction of high acid crudes (HAC). Upon the start of HAC processing, it is recommended that the measurements be repeated every three months (i.e. 1/3 of the points each month).

STANDARD VISUAL EXAMINATION

Conventional, non-intrusive NDE methods are typically not applicable to control valves and pumps because the cast structure and heavy wall thickness make ultrasonic evaluation ineffective and radiography impractical. However, the velocity-sensitive nature of naphthenic acid attack make both these components important to check, and a good "early warning" of the system corrosiveness as a whole. Critical control valves and pumps, which are identified in the initial Process Assessment, should be disassembled and inspected at shutdown opportunities. (This can even be undertaken with the plant on-line, by using the manual bypass or alternate pump whilst a valve or pump is examined.)

FIELD SIGNATURE METHOD (FSM)

FSM (by Roxar's ii-Corr divison) is a non-intrusive corrosion monitoring method that has some particular advantages for naphthenic acid monitoring. Corrosion measurements are made on the actual process component, as opposed to using a probe that measures the corrosivity of the process fluids.

Advantages of FSM are:

- It directly measures corrosion of the component (see figure 7 below)
- It is non-intrusive, so there is no concern about line or vessel wall penetrations, or probes causing turbulence-induced corrosion
- It is often installed while the equipment is running, so the user need not wait for a plant shutdown even for hot equipment
- The high temperature version of the system will readily handle the temperatures involved.
- Replacement of probes is avoided, as the technique measures the equipment itself instead of thin measuring elements that corrode.
- It can be configured to give quite sensitive readings over a particularly critical area (say an elbow, to ensure it survives the run), or it can sacrifice sensitivity but cover quite a large area (e.g. a section of packed vacuum column wall with suspect metallurgy, to ensure it is not badly corroding or cracking).

Disadvantages of FSM are:

- The initial cost is higher than ER probes, and there may be a significant ongoing cost for the vendor to help interpret the data.
- Refinery FSM systems are not currently configured to take readings continuously. A technician (trained by ii-Corr) would take periodic readings. ii-Corr could interpret these with a formal report, or by in-house personnel (see below).
- While FSM covers much more area than UT readings, it is not a global inspection/monitoring device. (There is no such single system).

Similar technology is also being provided by Foxtek.

CORROSION COUPONS

Corrosion coupons are the classic measurement tools for refinery corrosion monitoring. Corrosion coupons are very inexpensive and available from a variety of sources. We recommend that, in addition to the corrosion rate and a verbal description of any pitting, a photographic record be maintained before and after cleaning.

Coupons are not good where short-term effects dominate, because the coupon gives only an average corrosion rate over the entire exposure interval. For most equipment, coupons are typically installed and withdrawn at the scheduled unit shutdown. Coupons are a good compliment to ER Probes in lower velocity flow regimes (side cuts), and within the atmospheric and vacuum towers.

Fixed Ultrasonic Thickness Transducers

Measurements Application Areas:

- Wall thickness Corrosion/Erosion Monitoring
- Inhibitor Performance
- Scale and deposits.
- Separator Efficiency
- Solids Buildup
- Liquid film heights.
- Wet Gas Monitoring

Benefits / Technical Description

- No retrofitting necessary. Multi-channel data acquisition (4 and 8-channel)
- Insensitive to operating environment. Advanced signal processing software and high resolution
- On-line, real-time monitoring. Automatic scheduling of data collection
- Instantaneous on-demand inspection. Data repository and display options
- Easy to use Measurement. Precision: ±0.00005 inches
- Eliminates errors in manual data recording. High accuracy in Dt measurement – 1 ns or better
- High precision Standard transducers operate for temperatures up to 150 C
- Wide variety of applicable materials. Special transducers for high temperatures up to 500 C
- Multiple remote sites with centralized data acquisition. System pressure – no limit

Stream Sampling & Laboratory Analysis

Laboratory tests are not a realible method of detecting naphthenic acid attack, since the attack zone could be so localized that very little metal needs to be lost whilst a pipe or vessel becomes perforated. However, any significant increase in metal content above the base-case readings can be taken as a sign that attack that is more widespread is occurring.

Base-case information should be gathered from non-naphthenic runs, starting even before the next turnaround. There will be some evidence of background corrosion from general sulfidic and low-TAN mechanisms for the base case runs. For the crude and residue streams, there will be tramp corrosion debris from upstream oil field pipeline and transportation vessel corrosion. These measurements will

allow the engineers to assess the variability of the contaminant levels between crude batches, and permit the average background levels to be established.

The acidity of the crude and side cuts should be monitored with ASTM D-664 standard method for TAN measurements, using the electrometric end-point determination. This is required for black oils, where a colorimetric end-point is inappropriate. The same method should be used for the white oil distillates, to maintain consistency throughout the data series.

Metals analysis should include TOTAL iron and nickel, as well as the hydrocarbon-soluble portions. In most instances where naphthenic acid attack occurs, there is enough H_2S present to decompose any iron naphthenate in solution and to deposit solid FeS. This probably necessitates an ashing method of sample preparation, to obtain all of the metals in a uniform solution for analysis.

Side cut streams should be sampled for TAN, Fe and Ni counts. Fe is the best indicator of corrosion of carbon steel and low alloy equipment. Ni is the best indicator of corrosion of austenitic stainless steel equipment. Before blending with the high acid crude, the background values for Ni and Fe should be determined at the established stream sampling points.

On a weekly basis, monitor as a minimum, the diesel, and gas oil streams for the iron and nickel content. Additional streams may be necessary as determined in the plant assessment. An increase in Fe of 2-4 ppm above background or an increase in Ni of 0.1-0.2 ppm above background will indicate an increase in corrosion rates.

The following suggestions are offered to ensure that the stream sampling is accurate:

- Samples must represent the run on high acid crude, and should not be taken after the HAC campaign has terminated.
- Analyses must include all metals in the stream (specifically both soluble & insoluble Fe & Ni.)
- Analyze the TAN & metals in the crude and all the side cuts.
- Sample must represent the actual streams, not the sample piping. This means that the sample piping must be adequately flushed before grabbing the actual sample.
- Samples also need to be periodically taken at battery limits (Coker and Hydrotreater Units) to assure that the inhibitor is dispersed effectively to these limits.

CAUTION: The atmospheric tower overhead system and the vacuum tower overhead system are at an increased risk of corrosion when running high acid crudes, because of the degradation of naphthenic acids into lighter organic acids that end up in the overhead systems. These effects may be more pronounced at downstream plants, such as visbreakers and cokers. Where naphthenic acids may thermally decompose, lighter organic acids or carbon dioxide may form which can affect the corrosivity of condensed waters.

SECONDARY PROBLEMS THAT MAY ARISE WHEN PROCESSING NAPHTHENIC CRUDE OILS

DESALTING UPSETS

Naphthenic acids are capable of forming natural "soaps" when they are neutralized with inorganic cations, such as sodium, calcium, and ammonium ions. The soaps formed in this way exhibit surfactant behavior at an oil-water interface, such that the interface region in the desalter may become loaded with solids and emulsions. Some naphthenic crudes have thus acquired a reputation for causing desalter problems due to high conductivity in the vessels, and for producing very stable interfacial emulsion "rags".

Maintaining the acidity of the desalter effluent water in the range pH 5.5 - 6.5 can control the formation of naphthenate salts. If stripped sour water is used as the source for desalter wash water, this may not be possible when the stripped water contains high levels of ammonia. Such waters are produced when hydrotreater and FCC overhead water streams are fed to the sour water stripper plant. Therefore, the condensate and wash water streams from hydrotreater and FCC units should not be used in the desalters, when processing high percentages of naphthenic crude in the feed.

The problem is likely to occur only if the pH of the desalter effluent water is allowed to significantly exceed values above 8.0. This may sometimes be unavoidable when stripped sour water is used in desalting and the wild naphtha from gas oil hydrotreaters is added into the crude feed or upper pumparound return.

There may also be problems in plants where the sour water stripper (SWS) uses caustic soda to increase the ammonia removal. (Some units employ caustic injection in the lower part of the SWS column to expel the remaining ammonia, and the pH of the bottom water is made very alkaline – pH often above 10.0!)

The authors are aware of one refinery where caustic soda is deliberately added into the desalter wash water when processing Heidrun crude, with the intention to extract some of the acidity (reduce the TAN) from the crude if possible. There has been no adverse desalter consequences caused by this practice, although the effluent pH is only elevated to 6.5-7.0 maximum. The TAN reduction is minimal, but claimed by the refinery to be between 0.1 and 0.5 units. This level of caustic addition seems to not produce excessive quantities of naphthenate soaps or upset the interface controller discrimination. Whether the claimed TAN reduction occurs over a sustained period is also unproven.

New crudes from West Africa are appearing on the market, which contain large quantities of calcium naphthenate salts from the production stage. These are a known problem with the production operation for Kuito crude in Angola, where severe fouling of pump filters by calcium naphthenate is an inherent problem. Similar problems are expected, but to a worse extent, when the new Chad crudes are brought onto the market (DOBA). Even some North Sea crude oils (e.g. Heidrun) are known to generate such deposits.

One of the solutions that some producers are implementing for these oil fields is to add acetic acid to the crude in the hope of extracting the calcium as a water-soluble acetate salt. Excess quantities of acetic acid added to convert the calcium naphthenate will result in extra aqueous acid in the overhead condensate from the atmospheric distillation in refineries.

INCREASED AQUEOUS ACID CORROSION

The degree of hydrolysis of the calcium and magnesium chloride salts that remain in the desalted crude has long been reported to be increased by the presence of naphthenic acids in the feed.

Whilst such behavior could be compensated for in the atmospheric tower overhead with a neutralizing amine increase, or with increased caustic soda addition into the desalted crude, there could be a significant increase in the chloride content in the vacuum unit overhead condensate where no previous history shows this. There should be provision made for the addition of neutralizing and filming amines into the vacuum unit overhead if they are not already present.

The total acid loading in the vacuum unit overhead will increase due to the formation of light organic acids in the cracking of naphthenic crudes. This may be transferred into the atmospheric distillation when the vacuum overhead water is used as a component of the desalter wash water.

With organic acids present in significant quantity, the final accumulator pH will not be as high as normal. It will not be necessary to neutralize all the organic acids, but the portion of them that contributes to the strong acids (all of the formic acid and part of the acetic acid content) will need neutralization. Nalco's PATHFINDER® simulations should be performed using the analysis results from all overhead waters, so that the correct response can be determined. A good guide to the quantity of neutralizer needed is to add enough to bring the pH at 5% water condensed to just above pH 5.0. The remaining weak acids can be counteracted by proper use of a filming amine.

INCREASED FOULING OF EQUIPMENT

The reaction between the inhibitor and the existing sulfide surface films on the metal produces a complex structure of the iron polyphosphate / thiophosphate composition. This layer is tightly attached and resists attack from naphthenic acids. Some of the loose metal sulfide surface scales can become detached in this process, and are converted into metal – phosphorus compounds. This material has a higher density than the porous sulfide material, and tends to settle out faster in low-turbulence areas.

EXAMPLE OF RISK ASSESMENT DONE IN A REPSOL YPF COMPLEX IN ARGENTINA

By 2007, Repsol YPF started to consider the processing of a new crude available in the Argentinean market, with the particular characteristic of being very high in acidity, with a TAN greater than 5 (mg/ mgKOH).

Repsol YPF requested to Nalco an impact analysis of processing this new crude at one of their refining complexes. Observations and recommendations were made by our Nalco team with regard to processing this high acid crude (HAC).

The focus of the Nalco HAC Audit was to determine what impacts from processing a higher acid crude, such as PetroAndina, would have on the operational reliability of the refinery. The higher acid crude was going to replace partially existing low acid crudes.

Several factors cause naphthenic acid corrosion to be more difficult to predict than the traditional aqueous strong acid corrosion. Namely, naphthenic acid corrosion attack is very dependent on acid concentration, corrosivity of the acids, temperature, velocity, and metallurgy. It has been our experience that two refineries can process identical crude slates with similar metallurgy, but experience corrosion in somewhat different locations.

For many years, TAN has been the primary corrosion prediction tool used by refineries for predicting high temperature organic acid attack. TAN represents the total acids in a sample that can be titrated with KOH. Examples of components titrated by KOH are: H_2S, CO_2, organic acids, phenols, and naphthenic acids. A TAN titration is a simple and direct test, but it is influenced by a number of different acidic components. The high boiling distillate fractions will encounter different concentrations of these acidic species from the range found in the crude. Naphthenic acids may also concentrate in specific distillate fractions.

A plant visit was made in July 2007. Operating data, P&I drawings, and materials of construction for equipment and line sizes were supplied along with last inspection data available.

Conclusions & Recommendations

Based on the findings from the assessment done, Nalco identified several areas in the unit audited that needed to be addressed before the new crude PetroAndina could beprocessed routinely at a reduce risk. The addition of PetroAndina crude to achieve a whole crude TAN of 1.5 was the target agreed with the refinery, and it was predicted an increase in the high temperature naphthenic acid corrosion potential of the following circuits:

- Preflash Crude Circuit to Atmospheric Tower (including furnaces and transfer lines)
- Atmospheric Tower Bottoms Section

- Reduced Crude Circuit
- GOV Reflux Line

Recommendations included either upgrades in metallurgy, or treatment with a high temperature corrosion inhibitor.

The report also outlined the projected impacts on desalting, overhead corrosion and high temperature naphthenic acid corrosion from processing the projected PetroAndina crude blend.

EVAULATION

Feed Basis

Below is the crude slate of the existing base case and the Evaluation Case (18% Petroandina). The evaluation case was developed to target a whole crude TAN of 1.5.

Crude	**Base Case** m^3/hr	**Evaluation Case** m^3/hr
Current blend	300	247
PetroAndina	0	53

While the impact of the new crude PetroAndina on the Naphtha, Kerosene and GOL stream properties was minimal, it was a significant TAN increase for the whole crude, GOV and atmospheric resid. Below is a table that shows the impact on stream properties.

	Base Case				**Evaluation Case**			
Stream	Rate M^3/hr	Sp Gr	Sulfur	TAN	Rate M^3/hr	Sp Gr	Sulfur	TAN
Whole	300	0.87	0.71	0.62	300	0.88	0.73	1.50
Naphtha	18.2	0.74	0.07	0.37	15.0	0.74	0.07	0.37
Kerosene	29.1	0.8	0.05	0.03	25.5	0.8	0.05	0.06
GOL	71.1	0.8	0.33	0.05	62.4	0.8	0.32	0.19
GOV	36.7	0.8	0.90	0.48	36.7	0.8	0.81	1.43
Atm Resid	131.5	0.9	0.99	0.22	144.0	0.9	0.89	1.85

The increases in TAN for the whole crude, GOV and atmospheric resid have a large impact on the process risk. This is shown in the comparison risk assessment comparison with the base case (see Summary of Risk Assessment Output). [sal note: do we want to show a sample of the assessment output?]

Impact on Desalting

The addition of PetroAndina at 18 % was evaluated to see the impact on the desalters. The impact is shown in the Table below.

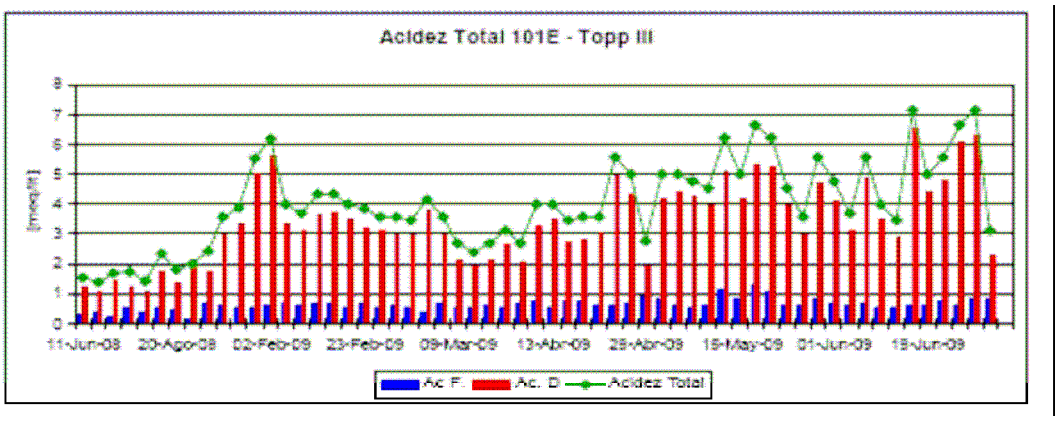
Crude Slate	Rate m^3/hr	% Design @ 115°C	% Design @ 140°C
Base Case	300	102	95
18% PetroAndina	300	120	115

Typically, desalters perform as designed up to 120-130% of design. At the charge rate target of 300 M^3/hr and desalter temperature of 115°C, the addition of PetroAndina crude was expected to provoke an increase the % over design from 102% to 120%.

Topping III Ovhd Corrosion Control

An increase in the TAN could increase the corrosivity of the tower overhead circuit. This would be the result of the increase in light organic acids. An increase in organic acids is a common observation when increasing crude TAN. The extent of the increase in the case evaluated was not predictable at the time when the audit was done, due to lack of experience in processing the crude under study.

After few months of being processed, the PetroAndina crude, an increase in the total acidity in the overhead system from about 2 meq/lt to 4,5 meq/lt, average was recorded, as could be seen in the graph below.



High Acid Processing Recommendations

Nalco assessment showed that there were several areas of concern and required action for processing PetroAndina with minimal risk.

Modifications were required for some of the circuits in the piping downstream of the desalter most were located around the furnaces.

All piping circuits downstream of the furnace outlet required some modifications or treatment. At a minimum, it was recommended these circuits were monitored closely as the TAN and temperature (>200°C) puts the risk regime into a *Moderate* rating.

Downstream of one of the furnaces to atmospheric tower was also an area where the risk increases from *Low-to-Moderate* to *Moderate-to-High*. Due to the *High* rating (downstream of the furnaces) these circuits and furnaces required metallurgy upgrade or chemical treatment.

The tower bottoms circuit and the short section of GOV piping had a *Moderate-to-High* ratings and was identified to need either a metallurgical upgrade or be chemically treated with an inhibitor.

The tower shell is 410SS lined at the flash zone to the bottom head and carbon steel. This section of the tower (GOV and below) was determined to be a *Moderate-to-High* risk and would require attention, either metallurgy upgrade or chemical treatment.

All exchangers and pumps were identified to be carbon steel or low alloy and not resistant to naphthenic acid attack.

Risk Assessment Criteria

Individual assessments incorporate factors for stream acidity, temperature, flow velocity, and plant metallurgy, together with the corrosion trends from the latest inspection sheets. The overall ratings for each part of the plant were reported in an Assessment Summary for each case.

Following is an example of the Assessment Summary from the survey of the units reviewed for each case. The summaries are broken down into discrete sections noted in the **Stream Section** of each page.

- **Risk assessment:** The risk factor is described based on the "likelihood of failure. A complete risk assessment would also incorporate consequences, which is beyond the scope of this audit. The risk factor is rated as "**High**", "**Moderate**", or "**Low**". To help further define the risk rating, please take steps in the following manner.
    - "**High**" (Action is required, either metallurgy upgrade or chemical passivation)
    - "**Moderate**" (Establish a rigorous monitoring program at a minimum)

  - "**Low**" (Generally no action is required unless the assessment case for the assessment is changed. Your routine monitoring program or a modified program may be needed.

- **Corrosion measurement:** Corrosion rates are a summary estimate based on the inspection data reviewed. While high temperature sulfidic corrosion tends to be uniform, naphthenic acid corrosion tends to exhibit both pitting and grooving attack. It is quite common for the highest metal loss due to naphthenic acid corrosion to be understated by ultrasonic thickness measurements. Because of this, additional wall thickness is typically allowed when considering the critical retirement pipe wall thickness.
- **Nalco experience:** The risk assessment is further qualified by Nalco's knowledge of similar equipment and conditions in the refining industry worldwide.
- **Temperature:** The typical higher temperature range of the section reviewed.
- **Velocity Ranges:** The typical velocity range of the section reviewed.
- **Wall Thickness:** The estimated original pipe wall thickness of the equipment reviewed.
- **Recommendations:** Whether to monitor, upgrade or treat with inhibitor based on the assessment results.
- **Monitoring:** A summary of monitoring recommendations
- **SCORPION® II Inhibitor:** A general assessment of the locations where a treatment program would be beneficial or where a treatment program likely would be useful after further evaluation. SCORPION is Nalco's tradename for their successful high temperature corrosion inhibitor.

Unit Section Surveys

Typical summaries are presented as showed in table below.

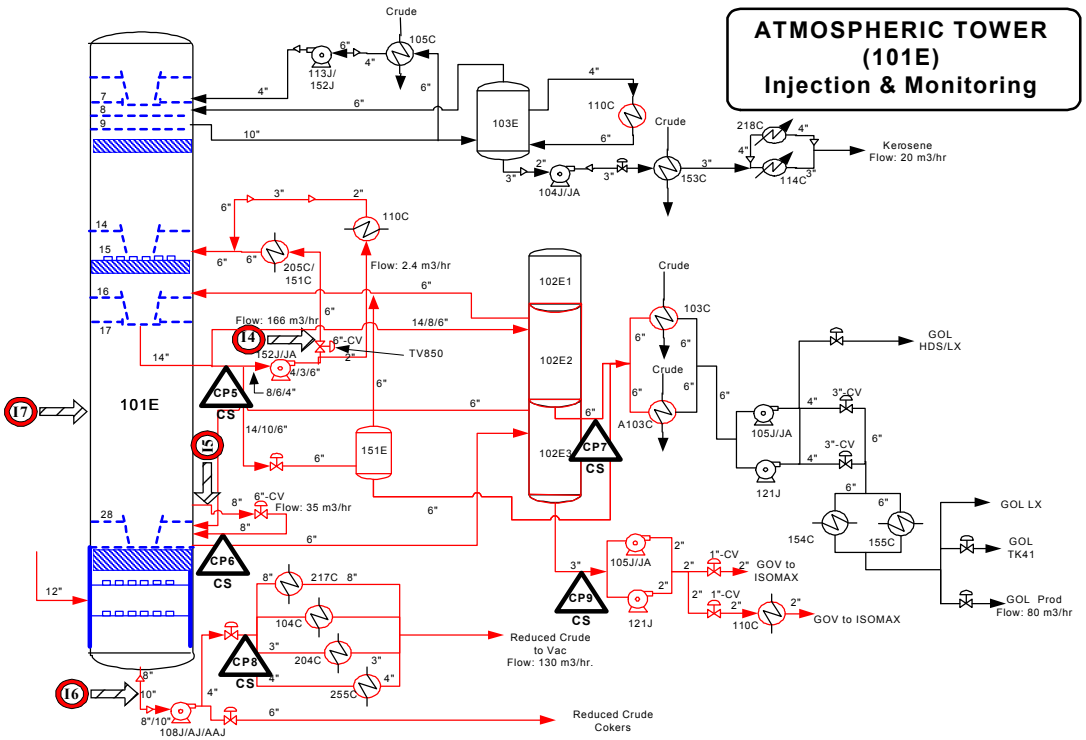
SECTION: CRUDE PREHEAT OUT OF DESALTER TO PREFLASH TOWER

Metallurgy:	Carbon Steel
Risk Assessment:	**Low**
Corrosion Measurement:	Most of the circuit has an assumed thickness of 3.8 mm (150 mil); No activity reported
TAN Estimate (Highest);	1.5
Nalco Experience:	Generally low

Temperature:	135-160°C
Velocity Ranges:	2.1-4.3 m/sec, liquid flow
Wall Thickness:	**Initial:** **Current Minimum:** good
RECOMMENDATIONS	
Monitoring:	Maintain current routine monitoring. No additional monitoring required at this time.
Corrosion Inhibitor:	No treatment plan recommended for this circuit. Although the tubes of the preheat exchangers XY may be at risk due to tube side temperatures.
Comments:	The operating temperature of less than 200°C and lower velocities should limit significant corrosion from naphthenic acid.

Monitoring and Injection Point Survey

Recommended locations for both SCORPION Inhibitor injection and circuit monitoring are shown on schematics which were based on the results from the Nalco risk assessment.



In addition, the lower section of the tower was also considered for an upgraded liner as inhibitor protection could be difficult above a certain tray due to a lack of any return streams coming back to the tower. Due to this situation, it was necessary to consider the installation of an injection point in the tower shell to allow good protection of the tower if upgrading of the tower internals were not done.

Locations for Field Signature Method (FSM) corrosion monitoring devices were identified for the furnace outlet transfer line.

Monitoring Locations / Methods

A list of monitoring locations and recommended methods are presented as part of the risk assessment. Below is a table showing some example from the audit done in the Repsol complex.

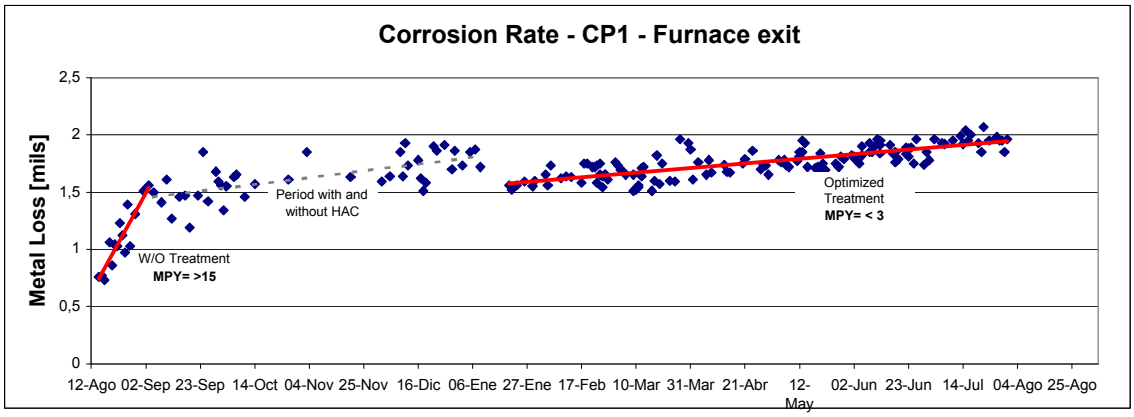
No.	Location	Method	Comments
CP1	Outlet of XZ Furnace	Corrosion Probe / Coupon (CS)	Nozzle and valve required
CP2	Piping downstream of FV100 control valve	Field Signature Method (FSM)	Nozzle and valve required
CP3	Outlet of XY Furnace	Corrosion Probe / Coupon (P5)	Nozzle and valve required

Chemical Injection Facilities

A list of chemical injection facilities are presented as part of the risk assessment. Below is a table showing some example from the audit done in the Repsol complex.

No.	Location	Circuit Protected	Injection Facilities	Comments
1	Downstream of the Desalter	➢ Tube of the XX, XY exchangers; furnaces, furnace transfer lines, exchangers and piping downstream of the XZ pumps; Tower bottoms.	➢ Nozzle and valve, Quill, chemical injection pump	➢ May not be required; recommend installing nozzle and valve only

As example of effectiveness, the graph below shows corrosion rate with and without treatment in one of the monitoring points.



CONCLUSIONS

Using risk based assessments before initiating the processing of high acid crudes can minimize the potential for compromising unit reliability. Risk based assessments combine both the understanding of Naphthenic Acid Crude behavior and operating experience to develop strategies to address those areas of a unit that require closer attention before and after processing begins.