

Design Guidelines for Chemical Treatments in Distillation Columns

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Introduction

Distillation is the application and removal of heat to separate hydrocarbons by their relative volatility or boiling points. This necessary addition of heat normally in the feed stream or at the tower bottoms via a reboiler can also lead to unwanted consequences such as polymerization, corrosion and reverse solubility. The removal of heat can lead to sedimentation, solubility effects, corrosion and precipitation. The concentration of certain constituents by the distillation process can cause corrosion, polymerization, sediment fouling and flow phenomena effects.

A properly designed distillation column can reduce the effects of these consequences, but in certain applications the polymerization, corrosion and other effects are very prominent leading to reduced separation efficiency in the column. This reduced separation efficiency increases the need for column maintenance and unit down time. In these applications a review of tower internal design and process chemical treatments should be initiated. Previously a review of tower internal design was published (1), whereas this article will discuss the application of chemical treatments in distillation columns.

Distillation Economics of Fouling

Distillation is the most widely utilized separation technique and there are basically two main types of chemical treatments in distillation columns; one is for corrosion control and the second is fouling control.

Distillation can be utilized in very clean services such as ethylene fractionation which, might fractionate for greater than ten years with no loss in efficiency due to corrosion or fouling - to very highly corrosive and fouling services. In Butadiene distillation, which is a highly fouling application, some fractionation applications are measured in days.

There are at least four types of chemical treatments in the process industry distillation.

1. Antifoulants which include dispersants, inhibitors, metal deactivators, retardants, antiscalants, and antipolymerants
2. Corrosion Inhibitors which include neutralizers, and both nitrogen and non-nitrogen-based filming corrosion inhibitors
3. Phase Separation Chemicals which include emulsion breakers, defoamers, antifoams, extraction aids, and solids-settling aids.
4. Scavengers which include agents to remove sulfides, oxygen, peroxide, and carbonyls.

Several general factors influence the corrosion or fouling potential of a distillation process. These include feedstock, temperatures, reboiler heat fluxes, and hydrocarbon residence time. The type of feedstock for a distillation column has a large influence on the fouling potential. Many crudes type have high higher fouling and corrosion potential than others. Feeds that have olefin or diene concentrations will have increased foaming and fouling potentials.

The general symptoms of tower corrosion or fouling are many but they may include;

1. Increasing or decreasing tower pressure drop
2. Inadequate separation leading to reduction in product capacity and purities
3. Tower temperature profile changes
4. Requirement to run the reflux rate higher or lower than design
5. Short reboiler run lengths
 - A. Increasing steam chest pressure
 - B. Increasing condensate temperature

- C. Increasing steam flow
 - D. Products not meeting specifications
6. Reboiler fouling and plugging
 7. Level control issues
 8. Instrument issues such as the leads line to instrumentation plugging

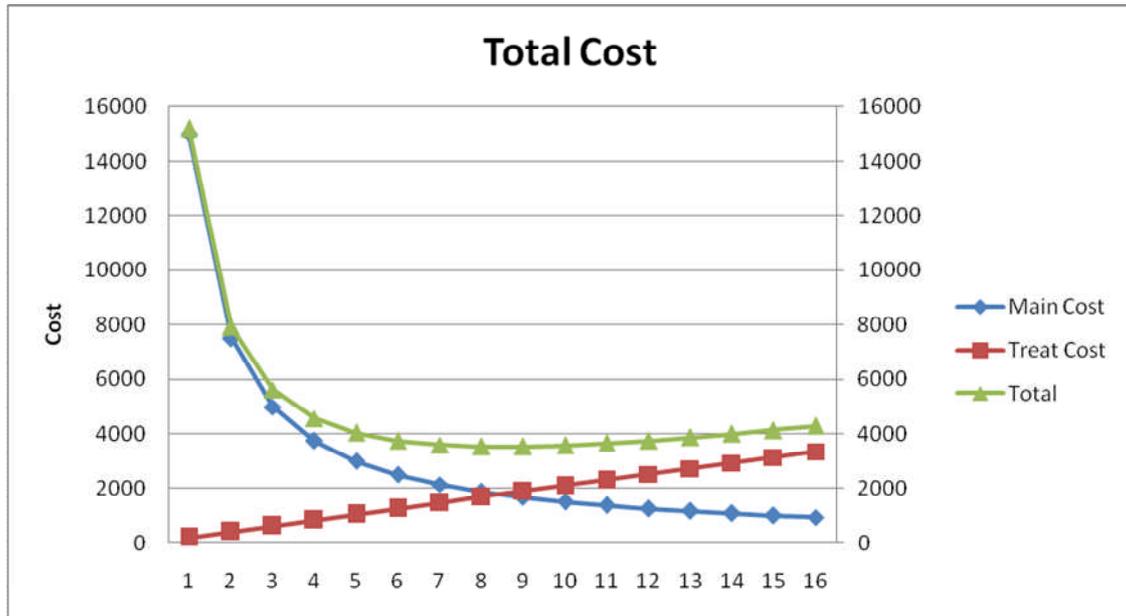
There are many benefits for utilizing chemical treatments, including increased capacity, reduced maintenance, and reduced environmental exposure leading to improved worker safety. By reducing the corrosion and fouling of a distillation column a tower may have higher separation efficiency. This increased separation efficiency can improved product quality while increasing capacity and production. Additionally increased separation efficiency can lead to lower energy consumption in reboilers and refrigerated condensers.

Reducing the corrosion and fouling of a distillation column will reduce turnaround frequency. In one case at an ethylene plant the DeEthanizer reboiler cleanings averaged 21 days, and with proper chemical treatments went to 8 months. The increased run length will reduce maintenance costs with the added benefit of reducing personnel exposure to carcinogenic chemicals found in fouling deposits while cleaning the tower or reboiler. Some species like butadiene and benzene have been shown to be carcinogenic. The species can be released when cleaning the tower and reboilers leading to unnecessary exposure to personnel. This benefit extends beyond the typical return on investment.

A typical return on investment for a chemical treatment programs should be 100%. If you extend your run length from one month to 8 months it can be as high as 1000%. Each chemical treatment program needs to be evaluated correctly to calculate the return on investment. The total maintenance cost of cleaning a tower or reboiler needs to be calculated and plotted against the cost of the chemical. Each cost is inverse to each other.

As chemical treatment increases, the maintenance cost decreases, but the chemical cost increases. The sum of the two costs will form a minimum at the optimum treatment dosage and maintenance interval. Environment considerations may shift this minimum to reduce potential exposure.

For example, if it cost USD 15,000 to clean a heat exchanger the maintenance monthly cost will be 15,000 divided by the number on months on line. Do not forget to factor in the environmental decontamination cost. If chemical cost is USD \$200.00 per month and increases 5% per month for each month of increased life, these two costs can easily be plotted to obtain the proper desired run length of the application. In this example energy cost was not considered.



The goal would be to achieve the calculated run length at the lowest possible cost. Treatment targets might be 10% residual chemical and 90% consumption of the chemical injected. It is a good practice to measure the residual chemical in the tower bottoms because of the reboiler circulation rate is much higher than most people envision. A typical reboiler will only have about 30% vaporization rate and can have 3 to 10 times the tower bottoms product flow rate.

A good rule of thumb is 25 ppm or less of chemical treatment based on the feed stream. This rule of thumb, like most rules of thumb depends on many factors such as the chemistry, concentration of the inhibitor and severity of the fouling potential.

Corrosion Control

Corrosion is a major issue in distillation equipment even with proper designs. Multiple factors can interact and create corrosive attack. With the current run length of plants between maintenance outages approaching five years, corrosion control is a must to maintain distillation efficiency and recovery.

Areas of corrosion in distillation include; crude distillation, vacuum distillation, and solvent extraction. Proper metallurgy selection and then proper chemical treatment is essential to prevent corrosion in the distillation equipment for hydrocarbon and chemicals processing.

Corrosion treatment chemicals include neutralizers, filmers, and other corrosion inhibitors. These chemical can prevent or mitigate damage from galvanic bi-metallic, aqueous acidic, and under-deposit corrosion, as well as pitting.

Crude Distillation

Corrosion in refinery crude distillation units is a common industry problem. Acids or salts present in the distillation column overhead system may cause corrosion when the right conditions exist. For this reason, it is common practice to inject corrosion inhibitors, neutralizer chemicals, or in some instances wash water to control corrosion in the column overhead system.

Crude Distillation Unit overhead corrosion diminishes unit reliability and operation in a number of ways. Some effects of overhead corrosion include equipment replacement and repair, lost throughput, reprocessing costs, offspec products, and downstream unit fouling. The two most common causes of overhead corrosion, acid corrosion and under salt corrosion stem from the presence of hydrochloric acid (HCl). Acid corrosion occurs when a condensed water phase is present and is most often characterized by a general metal thinning over a wide area of the equipment. The most problematic form of acid corrosion occurs when a pipe wall or other surface operates at a temperature just cool enough for water to form. HCl in the vapors forms an acidic azeotrope with water, leading to potentially very low pH droplets of water.

Here are some pictures from an atmospheric tower of a Residue Hydrocracker Unit. The trays were of monel metallurgy and in operation for eight years. They were inspected in October 2006 and found to be acceptable. Until 2005 the corrosion protection treatment was a combination of filming inhibitor and neutralizer. In 2005 the refiner decided to stop the neutralizer to save cost. This was the inspection result in March 2008. (4)

Under-salt corrosion occurs when corrosive salts form before a water phase is present. The strong acid HCl reacts with ammonia (NH₃) and neutralizing amines—both weak bases—to form salts that deposit on process surfaces. These salts are acidic and also readily absorb water from the vapor stream. The water acts as the electrolyte to enable these acid salts to corrode the surface. Pitting typically occurs beneath these salts. (3)

The principal agent causing overhead corrosion is hydrochloric acid, although amine hydrochlorides, hydrogen sulfide, organic acids, sulfur oxy-acids, and carbon dioxide can also contribute to overhead corrosion. Oxygen, introduced through poorly managed water wash systems can make corrosion worse.

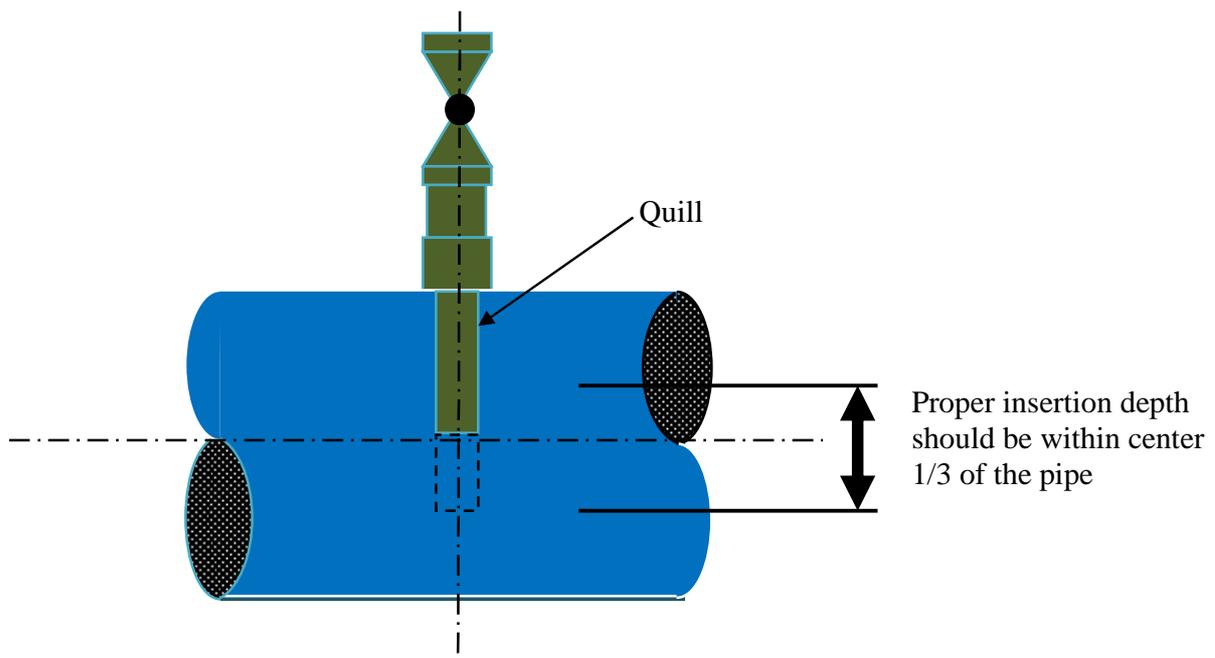
Hydrochloric acid induced overhead corrosion is primarily controlled by chloride management in the incoming crude oil and secondarily controlled by the use of supplemental injection of organic neutralizers and corrosion inhibitors in the overhead system. Chloride management consists of good crude tank handling, desalting, and then polishing/neutralizing with aqueous sodium hydroxide, which is commonly called caustic.

Refinery crude feeds contain water and inorganic salts (sodium, magnesium, and calcium chloride). Hydrolysis of calcium and magnesium chlorides (MgCl₂ and CaCl₂) occurs when crude oil is heated in the pre-heat exchangers and fired heaters. (2)

Many refiners inject caustic into the crude feed to the crude unit distillation tower to control condensation of hydrochloric acid downstream of the distillation tower in the overhead line. Caustic injection is carefully balanced with chloride levels measured in the overhead receiver.

Typically, operators specify chloride levels to be between 10 and 30 ppm. The lower limit is set to avoid over-treatment with caustic. Over treatment with caustic can result in contamination of the heavy products from the crude distillation tower with sodium, which can affect downstream units such as cokers, visbreakers, and Fluid Catalytic Cracking (FCC) Units. One best practice limits sodium to 25 ppm in the visbreaker feed.

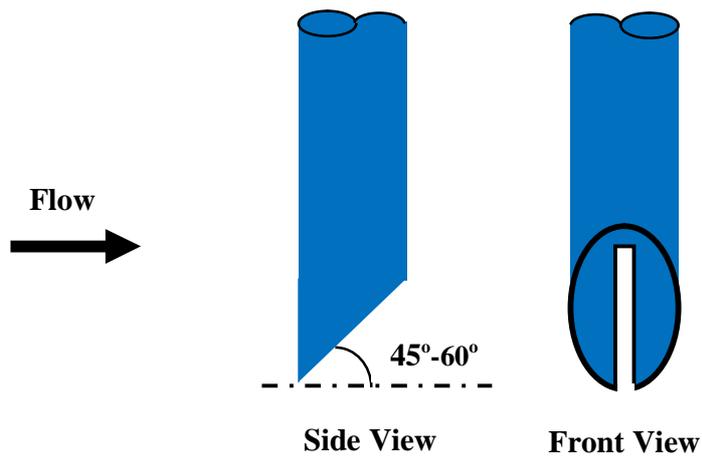
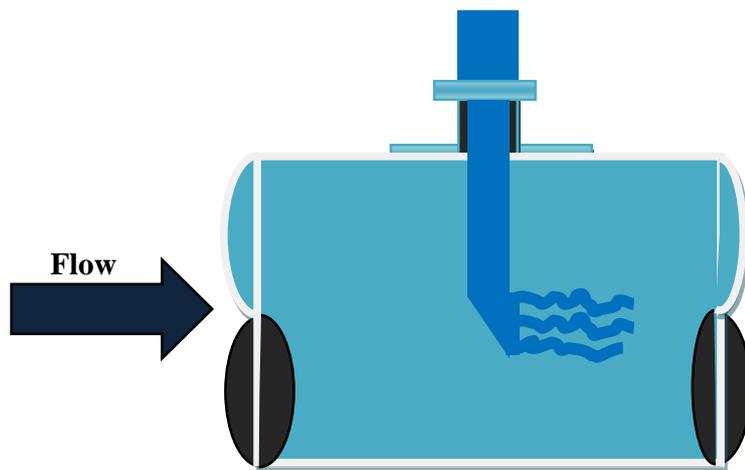
Caustic treatment has been ongoing for many years and the lessons learned from caustic treatment can be applied to other types of chemical treatments. How the chemical treatment is introduced to the process is very important to the success of the treatment. A typical injection quill might look like the following example.



Generally, the most effective position for chemical injection is at the center of the pipe. The highest fluid velocity is normally at the center of the line, therefore, injection at this point is intended to prevent concentration of the chemical at the edge where the velocity is low due to friction and will ensure efficient distribution of the chemical treatment.

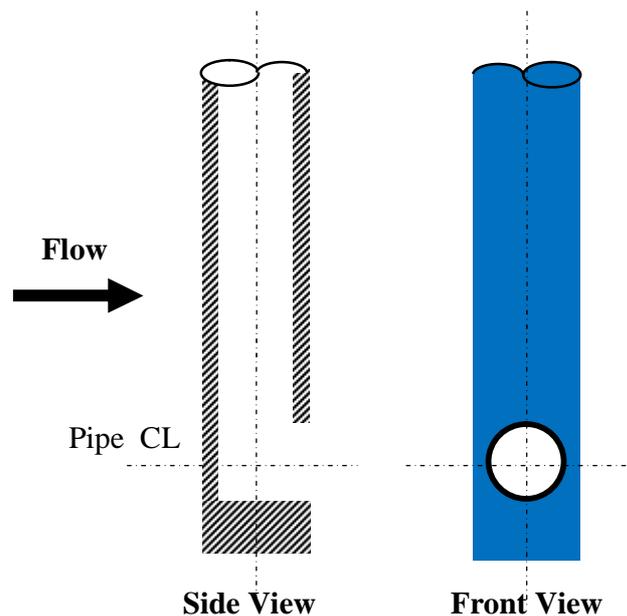
The design of a chemical injection quill uses an open end quill with a beveled tip that is slotted. The concept for this design is that the process stream pushes the treatment mixture through the slot in the quill which will create turbulence and mixing downstream. Moreover,

this design restricts the treatment flow to the pipe centerline area promoting mixing and dilution prior to contacting the pipe wall. It also is used to minimize the vortexes that form on the back side of a non angled quill. The angle and the slot minimize the down stream vortexes that are formed. If non-slotted some recommendations are to reverse the angle.



An example of a poorly designed chemical injection point can be seen in the next picture. The chemical was allowed to be injected close to the wall and the wall was thinned by the chemical.

The preferred design of a caustic injection quill is one that directs the caustic flow downstream, such as the side-hole quill, with the opening oriented downstream.



Naphthenic Acids in Crude and Vacuum Tower

Processing crude oils containing high levels of calcium naphthenates can present a number of operating challenges. Two processing technologies can help refiners successfully process these crudes. The first is a metals removal technology developed to remove calcium in the crude unit desalting operation and the second would be chemical treatments in the crude and vacuum columns. (7)

Several crude oils have come into production within the last few years that contain high levels of calcium naphthenates. Typically, these crudes are medium to heavy (specific gravity 0.89 – 0.95 kg/l), highly biodegraded oils, high in naphthenic acid content, and containing high concentrations of calcium ion in the formation water.

The calcium naphthenates found in many crude oils are largely insoluble in oil, water and solvents. Calcium naphthenates can cause fouling in separators, hydrocyclones, heat exchangers and other upstream production equipment. When blended into refinery crude oil

feedstocks, these crudes can create a number of processing and product quality challenges in the tank farm, crude unit and downstream units. These processing issues result from several observed attributes of crude oil blends containing calcium naphthenates :

- High conductivity crude blends
- Tendency to form stable emulsions
- High calcium content of atmospheric and vacuum resid
- Higher levels of low molecular weight organic acids in crude unit distillation column overheads
- Increased high temperature naphthenic acid corrosion activity

Higher Levels of Organic Acids in Crude Unit Overhead Systems

Processing crudes high in calcium naphthenates, as with many high TAN (Total Acid Number) crude oils, can result in higher loadings of low molecular weight organic acids and CO₂ in the upper portions of the crude and vacuum columns and overhead condensing systems. The amount and distribution of lower molecular weight acids and CO₂ in these systems is a function of the distribution of organic acid molecular weights in the crude oil, plus heater outlet, side cut, and column overhead temperatures.

The higher loadings of organic acids and CO₂ in crude unit distillation towers and overheads from processing high TAN crude oils may cause higher than desired corrosion activity in these areas. In some cases, the current means of controlling aqueous overhead or tower corrosion may be inadequate under these new conditions. Refiners may need to re-assess the capabilities of their overhead wash water systems, or have to utilize different corrosion inhibitor chemistries that are more effective under the new system conditions.

Where there are concerns about increased overhead system corrosion activities, refiners can use Ionic Equilibrium Model (IEM) technology to complete a unit aqueous corrosion control review. IEM is a proprietary process simulation-based technology developed by Shell Oil Products Company and licensed only to Baker Petrolite that rigorously models both the hydrocarbon and aqueous phases present in common refinery processes. The IEM utilizes a proprietary database of thermodynamic data for the phase behavior of neutralizing amines.

An additional concern for chemical treatment in the crude unit overhead is the application of the filmer technology. This filmer, commonly known as the corrosion inhibitor, forms a thin film on the metallurgy and prevents corrosion. However most of the commercial filmers have a certain surfactancy and can cause a water emulsion to occur in the naphtha product stream. The water in the naphtha stream can cause downstream unit problems, mainly corrosion issues. Proper selection of corrosion inhibitors to minimize this effect should be taken into consideration when refiners consider different filmer technologies.

Increased High Temperature Naphthenic Acid Corrosion Activity

Processing crude oil blends high in TAN can increase the potential for naphthenic acid corrosion in crude oil distillation units. This phenomenon has been well documented in industry literature. If not controlled, high temperature naphthenic acid corrosion can

result in higher equipment replacement costs, lower unit reliability and availability, and increased severity of downstream unit fouling due to elevated levels of iron naphthenates in crude unit distillates. Color stability may also be affected by the presence of iron naphthenates in crude unit distillates.

Naphthenic acid corrosion activity is dependent upon a number of key variables. The most important variables include:

- The naphthenic acid content of the hydrocarbon streams, typically measured by TAN (mg KOH/gram sample). Naphthenic Acid based corrosion is either reduced or augmented depending on:
 - a. Wt. % sulfur
 - b. Whether TAN is high or low
 - c. Whether fluid phase is liquid or vapor
- The temperature of the metal surfaces being contacted by the corrosive hydrocarbons
 - a. Naphthenic acids concentrate above 260 C boiling range
 - b. Highest concentration in 316-427 C boiling range
 - c. Lowest temperature where attack occurs ~200 C (400 F)
 - d. Above 450 C (825 F) disintegrates into lower molecular weight acids
 - e. Naphthenic acids corrosion activity is often high in location where acids condense out of the vapor phase.
- The shear stress of the hydrocarbon moving across the metal surface (a function of velocity and turbulence of the flowing stream)
 - a. At low velocity, acid concentration caused by boiling and condensing causes attack. Small erosion effect on corrosion if velocity is between 1.2-6.5 ft/sec.
 - b. At high velocity, multiphase stream rapid corrosion can occur due to erosion-corrosion. Naphthenic acid corrosion is accelerated in furnaces and transfer lines where the velocity of the liquid/vapor phase is increased. High turbulence areas have severe corrosion.
 - c. Turbulence and cavitation in pumps may result in rapid attack

- The type of alloy in use where hydrocarbon TAN, surface temperature and shear stresses make the system susceptible to naphthenic acid corrosion attack
 - a. Metallurgy - 316SS, 317SS and materials with higher alloys (more molybdenum) are more resistant to naphthenic acid corrosion.

Many areas of the crude distillation unit can be susceptible to high temperature naphthenic acid corrosion. These areas can most simply be identified as those which:

1. Are exposed to hydrocarbon fluids that contain corrosive levels of naphthenic acids (Generally considered to be any stream with TAN > 0.5 mg KOH/g, though lower thresholds apply in some cases)
2. Operate at temperatures of 220 – 400°C (425 – 750°F), and:
3. Are constructed with metallurgy not generally considered to be resistant to naphthenic acid corrosion attack. 316, 316L, 317 or 317 L stainless steels are generally considered to be resistant materials

Areas of the crude unit that are susceptible to naphthenic acid corrosion according to the above parameters typically include:

- Hot crude preheat exchanger network
- Atmospheric heater tubes
- Atmospheric tower transfer line
- Lower section of atmospheric tower (lining, trays) and associated atmospheric gas oil (AGO) pump around/product draw system
- Atmospheric tower bottoms line and any bottoms heat exchangers (if not integrated with vacuum unit)
- Vacuum heater tubes
- Vacuum tower transfer line
- Vacuum tower (lining, trays, packing) and associated LVGO, and HVGO pump around/product draw systems
- Vacuum tower over flash draw and “pump back” lines and associated equipment
- Vacuum tower bottoms line and heat exchangers

Other areas of the unit may also be susceptible depending on crude blend properties, unit design, operating conditions and actual materials of construction.

One of the greatest concerns refiners face when processing high TAN crudes is the potential for high temperature naphthenic acid corrosion attack. However, years of experience in this area have yielded several strategies that can be implemented to identify susceptible areas of the unit, to successfully mitigate naphthenic acid corrosion, and to effectively monitor this type of corrosion activity.

The first phase of an engineered solution is to perform a comprehensive high TAN impact assessment of a crude unit processing a target high TAN blend under defined operating conditions. An important part of the any solution system is the design and implementation of a comprehensive corrosion monitoring program. Effective corrosion monitoring helps confirm which areas of the unit require a corrosion mitigation strategy, and provides essential feedback on the impact of any mitigation steps taken.

With a complete understanding of the unit operating conditions, crude oil and distillate properties, unit metallurgies and equipment performance history, a probability of failure analysis can be performed for those areas which would be susceptible to naphthenic acid corrosion. Each process circuit is assigned a relative failure probability rating based on the survey data and industry experience.

Corrosion inhibitors are often the most economical choice for mitigation of naphthenic acid corrosion. Effective inhibition programs can allow refiners to defer or avoid capital intensive alloy upgrades, especially where high TAN crudes are not processed on a full time basis. Baker Petrolite has pioneered the use of low phosphorous inhibitor formulations in refineries where the potential downstream effects of phosphorous are a concern. Use of Best Practices for high temperature inhibitor applications ensures that the correct amount of inhibitor is delivered safely and effectively to all of the susceptible areas of the unit.

Crude blending is the most common solution to high TAN crude processing. Blending can be effective if proper care is taken to control crude oil and distillate acid numbers to proper threshold levels.

Fouling Control

Several general factors influence the distillation fouling potential of a process. These include feed stock, chemistry, temperatures, reboiler heat fluxes, and hydrocarbon residence time. The type of feedstock for a distillation column has a large influence on the fouling potential. Feeds that have olefin or diene concentration will have increase foaming and fouling potentials.

The column operating temperature affects fouling rates. In a refinery the crude unit and hydrotreater units might have towers that run under a vacuum to reduce the bottoms operating temperature to reduce fouling and product degradation. In an ethylene unit a DePropanizer tower might have the overhead cooling be refrigeration to reduce the tower bottom temperature. The goal would be to operate the column below the fouling initiation temperature of the contained fouling species.

For highly fouling services restrict the reboiler heat flux. A typical reboiler might have as much as 30% vaporization and high heat fluxes. Reducing the percent vaporization and using a lower heating medium will reduce fouling potential. The hydrocarbon residence time will affect the fouling rate. Design columns to have lower residence times in fouling services. At lower charge rates residence time is increased, minimize low charge rates when possible.