An Integrated Approach to Overhead Corrosion

GE Water and Process Technologies
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Introduction

In today's global refining market, there is often a tremendous incentive to maximize distillate production. Unfortunately, the same thermodynamic conditions that allow a fractionator to make more diesel, also lead to lowering the deposition temperature for amine-hydrochloride neutralization salts. Increased deposition of amine salts leads to dramatically more aggressive corrosion conditions. This situation puts the profits available for maximizing diesel production in nearly direct opposition to reliability. Decisions surrounding such economic tradeoffs can be difficult to make quantitatively with traditional methodologies.

Variability is the new constant

Processing shale crudes can make the challenges outlined above even more difficult. This is because these crudes themselves are highly variable (**Figure 1**). These opportunity crudes are often treated with amine-releasing H2S scavengers or other production field chemicals, and also have distillation yield curves very skewed to the light ends (**Figure 2**). These factors all contribute to challenges, with respect

Figure 1 – Several different batches of shale crude recieved on the same day. Variability in crude charge causes corrosion challenges in the overhead.

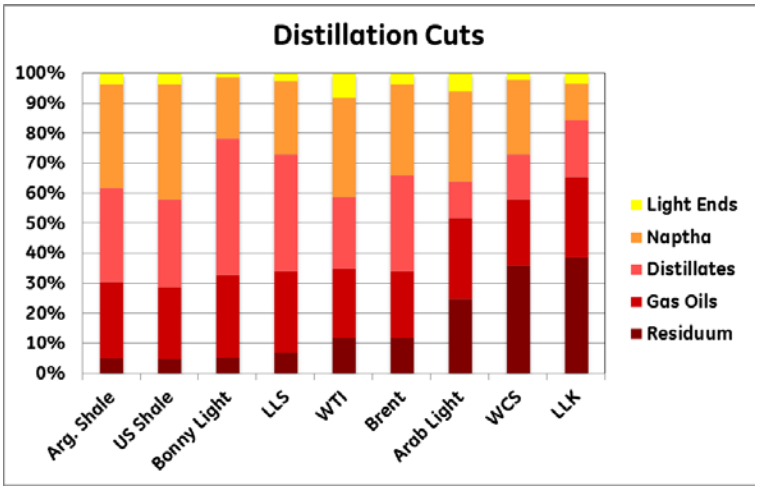

Figure 2 - Comparison of yield distributions for shale crudes.

to managing corrosion in the overhead.

The primary drivers for corrosion in the overhead of an atmospheric fractionator are well understood. **Figure 3** schematically shows the primary drivers. In refineries seeking to process opportunity crudes, knowledge of the drivers, advanced metallurgies, and traditional feeds of neutralizers and filmers may not be enough to alleviate aggressive salt deposition and its associated corrosion. Units designed for cracked spreads and fuel demographics from decades long gone are ill suited to making distillate without simultaneously making it easier for these aggressive salts to deposit.

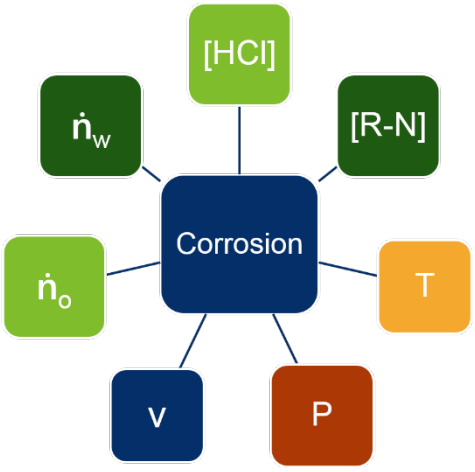

Figure 3 – Primary drivers for overhead corrosion

A typical refinery will have anywhere from three to 10 amines circulating in its various fluids. Any of these can have the potential to salt at deposition temperatures above the water dew point and become problematical. **Figure 4** details a deposit analysis from a failed pump-around exchanger at a US Gulf Coast refinery. The overhead system had experienced 3 corrosion-related failures within a 2-year period. Prior to that time, they had not experienced an unplanned corrosion event for decades. The results of the deposit analysis revealed that the neutralizing amine showed the highest concentration; the second highest was the plant amine used for acid gas sweetening and coming in via the slop-oil system; and the third highest amine concentration was from an H_2S scavenger treated crude oil source. The plant had previously been unaware of the amines from the H_2S scavengers. The plant had maintained good desalter performance and chloride control in the overhead, yet the elevated amine concentrations increased the salt formation temperature to the point where it formed in the tower's top pump around section, resulting in the high corrosion rates.

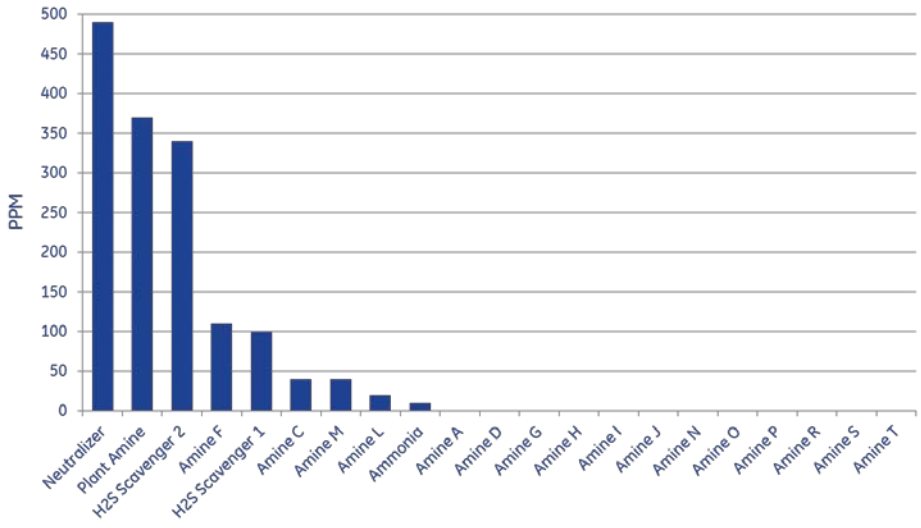

Figure 4 - Typical amine distribution profile.

As illustrated with the case study above, the impact of salt-deposition can be severe. The example below, on the other hand, shows how GE assisted a refiner in defining a new operating envelope in order to limit such overhead corrosion and improve the unit's economic balance. First, the relationship between and the salt-point and the water dew-point was

calculated using an ionic equilibrium overhead model. The model used was GE's proprietary "**LoSalt Ionic Equilibrium Model**". This model is based on the **Aspen Plus™** process simulation engine, but also uses proprietary GE property databanks, a custom interface, and custom calculation engines. In the example above, corrosion in the overhead was identified and quantified by overlaying the data with operating conditions. Each of the bars in **Figure 5** represents the temperature difference, in degrees F, between the water dew-point and the salt-point.

The blue bars represent measurements where the water dew point is 10°F or greater than the salt point temperature. Yellow indicates 0-10°F differential. The red bars are instances when the salt-point actually fell below the water dew-point in the system. Prior to December of 2010, the refiner had experienced very high corrosion because of several instances when the salt-point dropped below the water dew-point. Recognizing the impact salt-point had on corrosion control, the output of the ionic equilibrium model was then used to establish a new, safer operating envelope to minimize system corrosion. Since that time, corrosion rates have been maintained at 5 mils per year or less, and the operating envelope is actively managed based on the calculated salt points as the system conditions change.

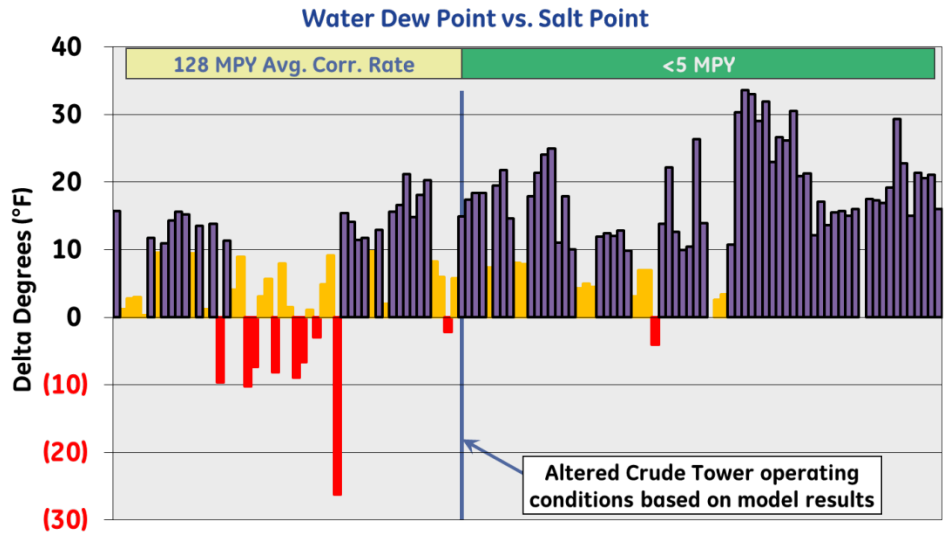

Figure 5 - Corrosion impact illustrated by salt occuring over the water dewpoint.

What is not apparent to many refiners, is that the relative ordering of circulating amine concentrations, and their potential to precipitate, are not constant. In fact, both amine identity and concentration vary significantly on a variety of time-scales. **Figure 6** shows an example of actual amine concentrations measured at another US Gulf Coast refinery. What this shows is that on each row, which is an individual day, a sample was obtained over a one month period. In this case, the potential is demonstrated for different amines to drive salting behavior on different days. A cell that is highlighted yellow, is present in a concentration sufficient to induce salting at prevailing conditions. This table importantly illustrates that on any particular day, anywhere from one

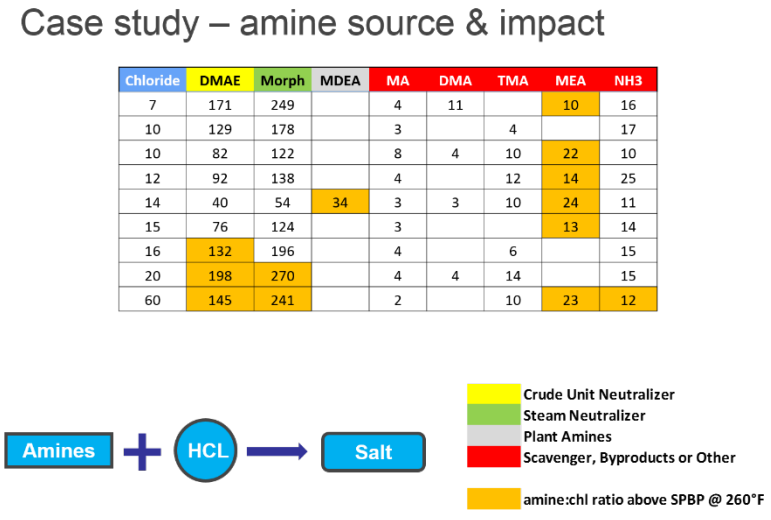

Figure 6 - Amine diversity and sample-to-sample variation.

to four amines can contribute to salting, and they do not necessarily have the same identities. Oftentimes, it is said that these amines are coming in with the crude and so must simply be accepted. While this is sometimes true, the amines coming in with the crude themselves are generally at a level in which they can be handled by a properly designed unit. What makes the amines so problematical is their tendency to recycle in the refinery, which contributes to the growth of steady state concentrations over time in many locations. When cycling up, these amines frequently reach levels well over what is expected if one were to consider only the amount in the crude, and single pass behavior. **Figure 7** shows the results of an amine mapping exercise, wherein the recycle pathways through the refinery can be determined. Once these pathways are made visible, then mitigation strategies can be developed in a systematic and prioritized way.

New Technologies to Deal with Variation

Traditional methods, such as outlined in the previous sections, have been used for decades to improve salting behavior in refineries. Unfortunately the industry today faces a nearly perfect situation to induce salt based corrosion at unprecedented levels. This is because of the high levels of amines present in today's opportunity crudes, but is also driven by the combined global emphasis on diesel fuels and the legacy designs of refineries. Most modern refineries are not properly designed for the throughputs,

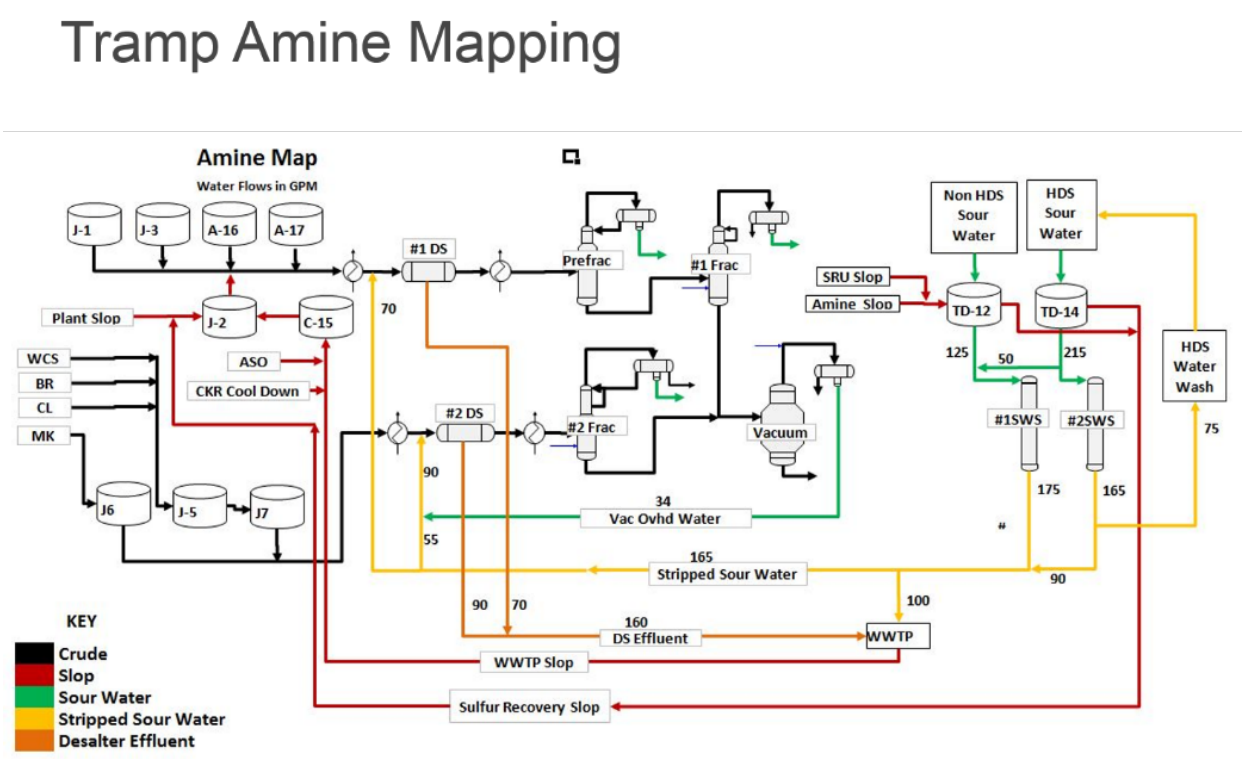

Figure 7 - Amine mapping study.

operating conditions, product mixes, crude compositions, and variability in play today.

In order to better handle the challenges around salt point deposition and variability outlined above, we must use new tools to provide better visibility into the variation itself, and its primary drivers. **Figures 8** and **9** show a new online corrosion monitoring system, web-based interface, and online control devices. These devices are all targeted at crude unit atmospheric fractionators. The system allows the measurement of online pH and can also be used to control a neutralizer pump in an automatic way.

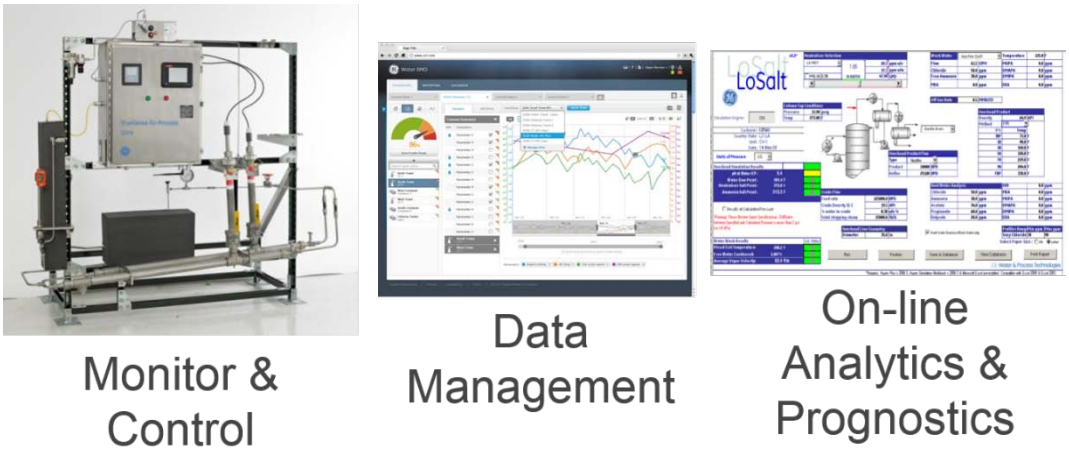

Figure 8 - New tools allow unprecedented visibility into corrosion dynamics

Figure 9 - Online telemetry opens new capabilities

Additionally, there are options for continuous online chloride measurement, as well as ports for electrical resistance (ER) probe signals into the unit. These telemetries then become the basis for sophisticated control schemes and engineering calculations. When so configured, the system offers simultaneous automatic monitoring of pH and chlorides, control of the neutralizer, caustic, and filmer pumps, or any combination thereof.

The system above allows critical telemetry to be historized and fed into new online tools that can automatically compute salt-point and water dew-point. These calculations are performed from base principles using proprietary algorithms, running on GE's **Insight**™ Platform. Additionally, data analytics and prognostics engines can be used for sophisticated analysis.

Figure 10 shows how the typical variability in overhead pH can be eliminated by using automatic control of the neutralizer pump. While such a scheme is not enough to eliminate corrosion problems in many cases, it does become a powerful tool in an integrated approach to advanced corrosion control methodologies.

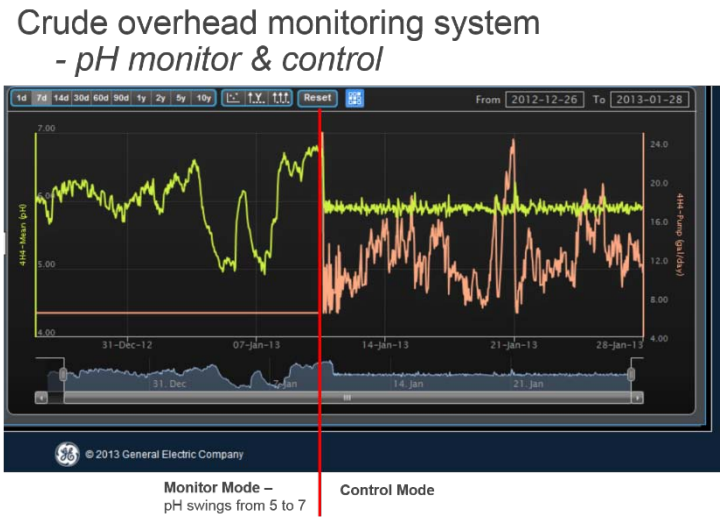

Figure 10 - pH variability can be eliminated via automatic neutralizer pump control.

The availability of large amounts of operational, laboratory, and salt-point data with full amine granularity allows unprecedented visibility into salting and/or corrosion dynamics as we will begin to show. As an example, **Figure 11** shows a typical daily pH and chloride monitoring scheme drawn as red dots on the chart. Observing only these points would lead one to believe that corrosion metrics are consistently within their control ranges. Only when full online measurement of these metrics are enabled, shown in blue, is it apparent that there is much variability that would be expected to cause previously unobserved salting and corrosion episodes.

Eliminating the variability in pH and chlorides is a great first step to holistic corrosion control. These projects and equipment can then be used to eliminate two primary sources of variability driving episodic corrosion. While these are powerful steps helping to reduce corrosion drivers, they may not be enough to eliminate all problems in many cases. Amines are increasingly recognized as another primary driver of variability dramatically affecting overhead salting and corrosion. As discussed previously, these amines cycle up in a refinery and often present significant problems in the overhead. Oftentimes as many as 4-5 amines can be significantly contributing to salting in the overhead system in any brief period of time.

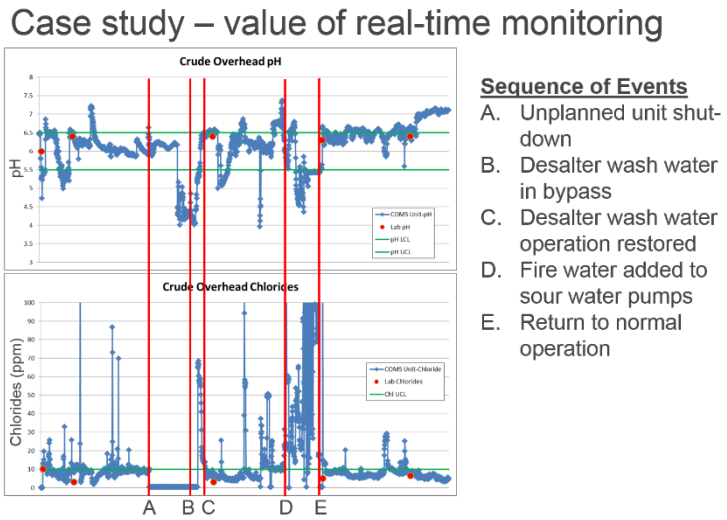

Figure 11 - Online capability reveals large numbers of previously unseen chloride spikes. This firmly illustrates the maxim that 90% of damage can occur in 10% of the time.

Figure 12 shows data from a typical refinery. This data shows significant variability in sample-to-sample amine speciation. It is important to realize

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that only three of the detected amines are primarily contributing to the corrosion issues at hand. The top 3 amines driving corrosion during this timeframe are amines 1, 3, and 4. **Figure 6** shows that the random gyrations of these amines often dictate that it is a different species, or set of species, driving corrosion from one sample to the next. Understanding these statistical amine dynamics is critical to mitigating their impacts on corrosion.

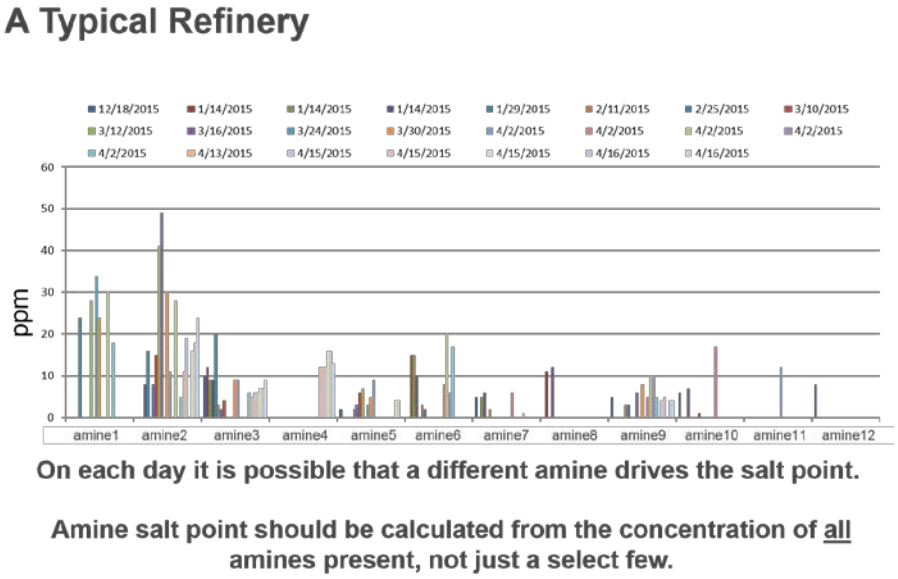

Figure 12 - Amine concentration histograms for 23 samples collected over a 4 month timeframe.

Towards an Integrated Approach to Overhead Corrosion

Traditionally the impacts of amines in the overhead have been considered as a series of snapshots, or "what-if" scenarios. Unfortunately this methodology suffers from several primary deficiencies. In order to mitigate corrosion in the overhead in a holistic way, it is important to understand how the unit operates over time, and simultaneously under the impact of these multiple sources of variation known to drive salting behaviors.

Figure 13 shows that the random gyrations for observed amine concentrations oftentimes obey well known laws of probability and statistics. This means that we can use these data, and new methodologies, to derive expectation values and variances for total salting frequency and associated corrosion mitigation schemes. Furthermore, this can be done in an actual operating crude unit evolving under the influence of multiple degrees of variation.

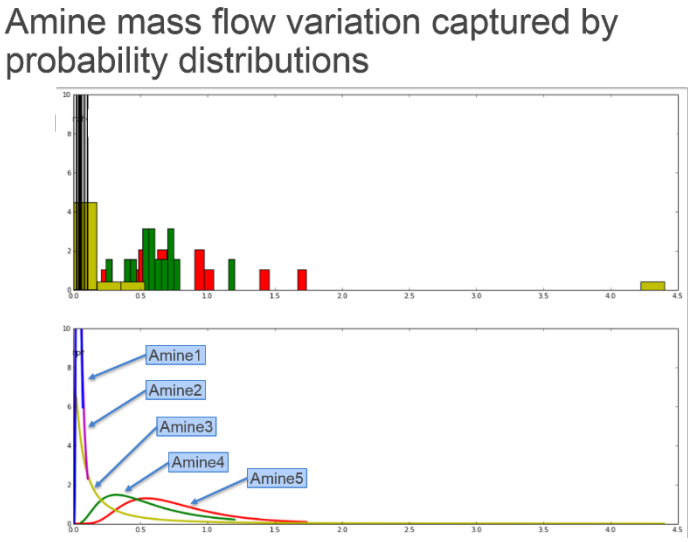

Figure 13 - Amines in refineries often exhibit classical pseudo-random behavior.

By looking at the variability for operations of the unit over time, and the variability of amines and chlorides, we can then derive a statistical formulation of salting behavior. **Figure 14** shows measured salting behavior for MEA Hydrochloride in an atmospheric overhead. This data was collected over approximately a one year timeframe. During this time, the

unit was run under several different operational modes. Salt Point Boundaries can be observed for operations at 4 critical temperatures. Two important points can be made about this data. First is that higher operating temperatures do not always correspond with higher salt points, and second is that even at the most forgiving operating conditions, significant incidence of salting episodes are exhibited. These factors definitely have an impact on unit reliability.

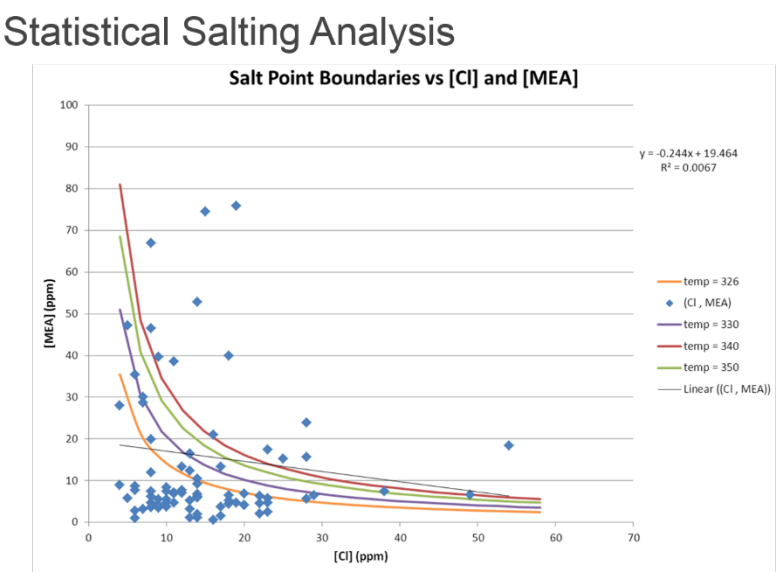

Figure 14 - Data showing MEA hydrochloride salting over the water dewpoint with high frequency. Points laying to the right of these curves indicate salt deposition over the water dewpoint. Salts underneath and to the left, indicate no tendency for salt depostion.

While the chart in **Figure 14** can be used to manually derive salting frequencies for a single amine, other methods can be used to quantify and analyze data based on usage of large data-sets inclusive of all amines cycling in a particular system. Advanced analysis techniques can unlock tactical and strategic options that were previously not apparent. Results from such analysis can have great value to a refining organization if used properly.

Figure 15 shows an example of one such technique as applied to salting behavior in a typical unit. By appropriate analysis, more effective ways to operate a unit to a desired product mix can sometimes be ascertained. Once more reliable modes of operation are discovered for a given set of crude diet and product mix objectives, then projects and capital can be deployed to better mitigate corrosion risk from an engineering perspective.

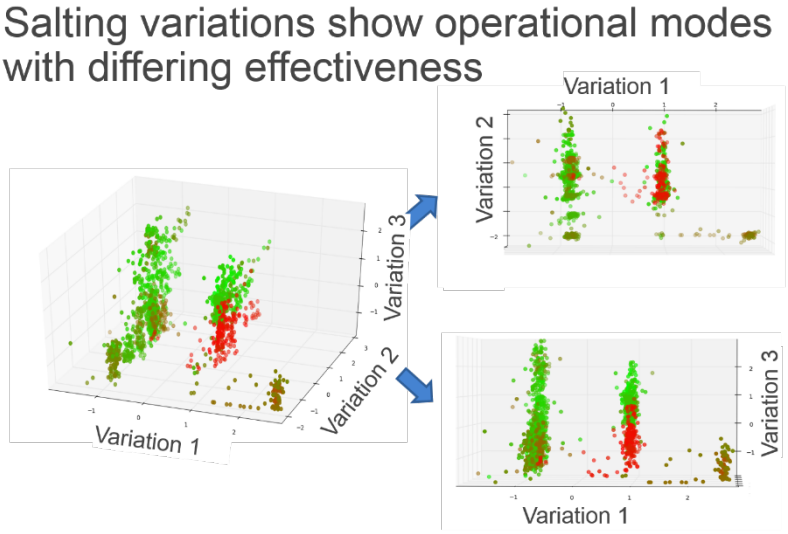

Figure 15 - Previously hidden operating regimes can be unlocked for given product strategies.

Summary

In today's refining landscape, more effective ways are needed to mitigate corrosion. Units under continued exposure to episodic variations from shale crudes, and other opportunity crudes, can often experience significant corrosion that goes undiagnosed and unmitigated using traditional techniques. New methods are available that can provide unparalleled clarity towards the chemical and operational drivers for corrosion in the overhead today. This clarity then opens options for

data driven decisions around the use of chemical additives, unit operations, and deployment of capital. Only by a combined holistic approach to overhead corrosion control can some problems be effectively addressed.