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think simulation | getting the chemistry right

Minimizing corrosion in refinery overhead systems

Using simulation to understand amine – HCl phase changes

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Introduction

OLI Spotlight Seminar

Corrosion in Crude Distillation Unit (CDU) overheads

Corrosion is a major issue in Crude Distillation Unit (CDU) overheads as well as other unit overheads in refineries. Even though hydrochloric acid attack is a well understood refinery process, its effects in the overheads when combined with neutralizing amines is particularly serious. Corrosion related failures in the overheads cause unplanned shutdown time or fouling, impairing operations reliability. Using ionic modeling to minimize the formation of corrosive amine HCl liquids / solids in the overheads brings significant savings and reduces the possibility of down time.

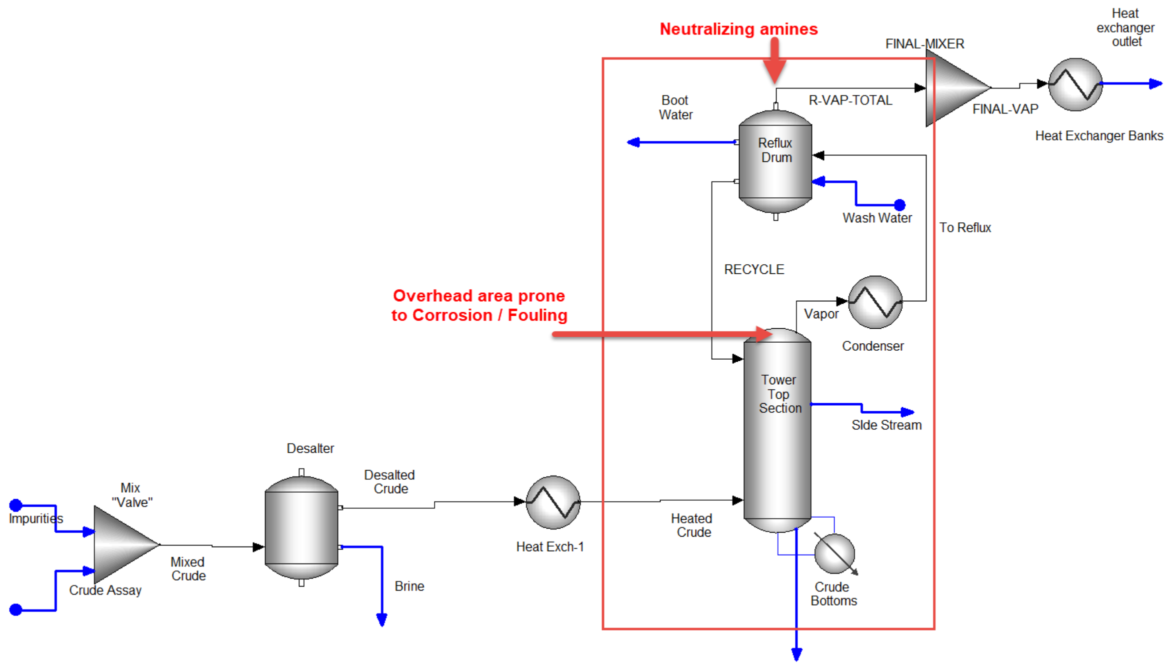


Figure 1. CDU and overheads simulation

The red box in Figure 1. indicates the area of focus. The arrows point to areas susceptible to corrosion or fouling. It is usually seen in pump-around areas or the top trays of the distillation units. Neutralizing amines are added to combat corrosion in the refinery crude overhead systems. However, under-deposit corrosion can also occur from amines – HCl components either condensing or sublimating above the water dew point in the overheads. Chlorides can be present even in the desalter output, and tramp amines as well as the neutralizing amines may be part of the overhead streams.

Key chemical reactions involved

Looking more closely at the chemistry of under-deposit corrosion, first we can see how HCl can form. The salts that the desalter does not always remove can hydrolyze with water at high temperatures according to reactions like these:

$CaCl_2 + 2\ H_2O \rightarrow 2\ HCl + Ca(OH)_2$

$MgCl_2 + 2\ H_2O \rightarrow 2\ HCl + Mg(OH)_2$

Then, amines tend to react with the HCl under the "right conditions" to form amine chlorides which can lead to under-deposit corrosion:

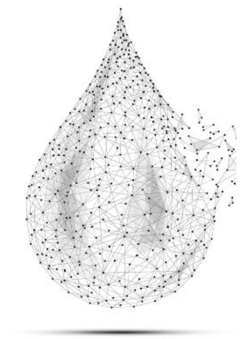
$RNH_{2(v)} + HCl_{(v)} \rightarrow RNH_3Cl_{(s/l)}$

$RNH_3Cl_{\ (s/l)} + H_2O \rightarrow RNH_3^+{}_{(aq)} + Cl^-{}_{\ (aq)}$

In other words, amines solve one kind of corrosion problem in overheads and can also be part of the problem! To avoid under-deposit corrosion caused by the amine + HCl reactions noted above, ionic modeling – that is, electrolyte thermodynamics models – can determine at which conditions the amine – HCl reaction takes place, and avoid operating at that temperature.

Ionic modeling to calculate safe operating temperatures

For a typical overheads stream composition, shown in Table 1. on the following page, ionic modeling can determine safe operating temperatures by calculating the phase change temperature of the stream. When ionic modeling was first used to determine this temperature, this was called seeking the "salt point."

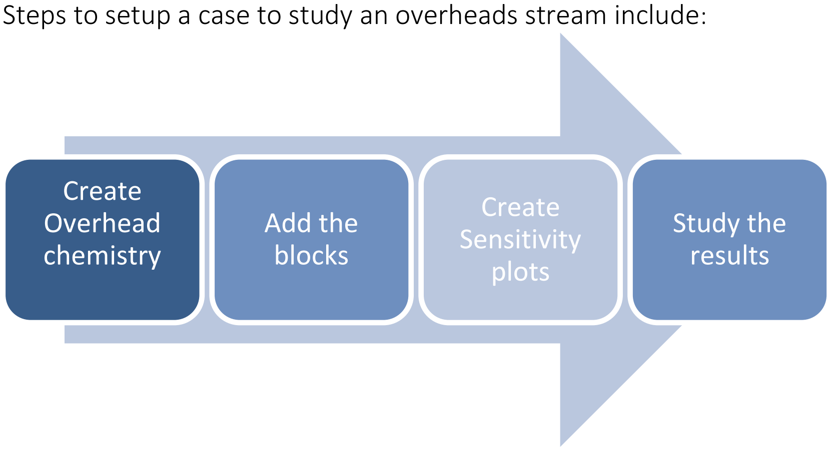


In later work, Kathleen Willis and Rusty Strong introduced a more rigorous description of ionic dew point in relation to salt point and water dew point. These definitions made an important distinction between the term salt point and ionic dew point. Even though salt point is a temperature at which the solid salt forms, ionic dew point plays a critical role in determining possibility of corrosion in the overhead system. Ionic dew point tells us at what temperature the highly concentrated Ionic liquid will appear and where it happens when compared to the water dew point. Ionic dew point occurs because of ionic attraction between ammonium & chloride ions and water and also due to the partial pressures of ions in the system.[11]

Spotlight case study

To illustrate how ionic modeling can be used to determine the ionic dew point, the salt point and the water dew point, we will develop an illustrative case study. The study in this paper uses OLI Flowsheet: ESP as the flowsheet simulator; however, OLI as a property method within any one of OLI's Alliance Partner products will produce the same results.

Steps to setup a case to study an overheads stream include:



[1] Strong, R. & Wills, K., (2015), "Crude unit overhead corrosion control successfully driven by ionic modeling," Presentation, NACE CORROSION 2015

We would create an overhead chemistry using the component descriptions found in Table 1. Amines used will be morpholine and cyclohexaneamine.

Typical chemical makeup of an overheads stream
H_2o
Alkaline hydroxides (MgOH, NaOH, etc.)
Salt chlorides ($MgCl_2$, $CaCl_2$, etc.)
H_2S
Hydrocarbons
HCl
Assays and pseudo components
Amines and ammonia

Table 1. Typical chemical overheads makeup

For the step of adding the blocks, we could use the same layout as seen in Figure 1. on the first page, or we can shortcut the simulation, ignoring the actual column distillation and instead focusing only on the stream leaving the overhead unit and the cooling / accumulation process.

Creating the sensitivity plots requires some explanation. In this particular case study using OLI Flowsheet: ESP, the sensitivity plots are developed using a mixer to model the top of the column, and then the mixer temperature is varied to study the effects of the change of temperature on water vapor formation, liquid water condensation, ionic liquid formation and solid phase formation.

Sensitivity plot results

This technique produces the following plots in our final step of studying the results:

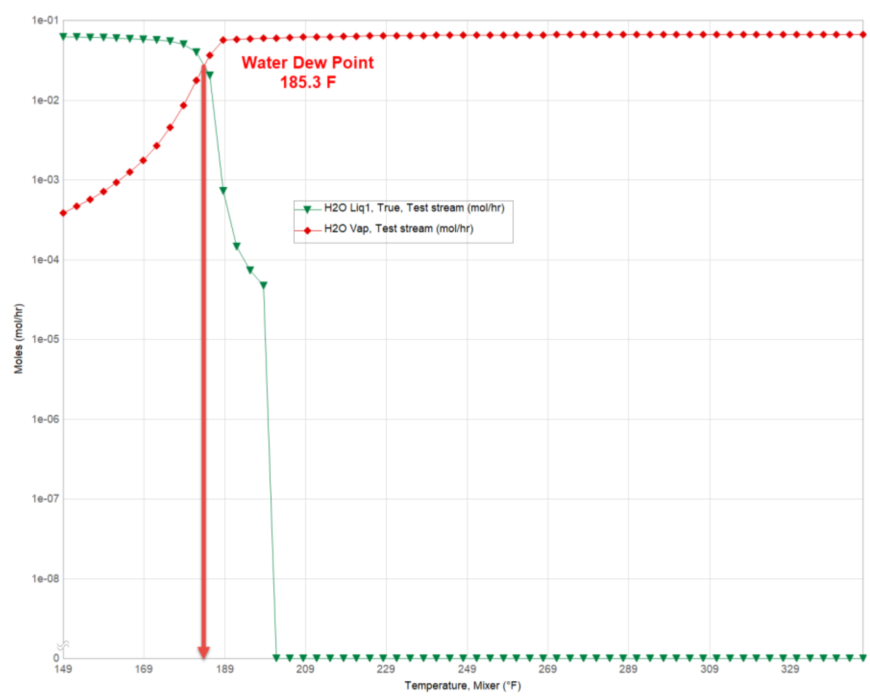


Figure 2. Detecting the water dew point

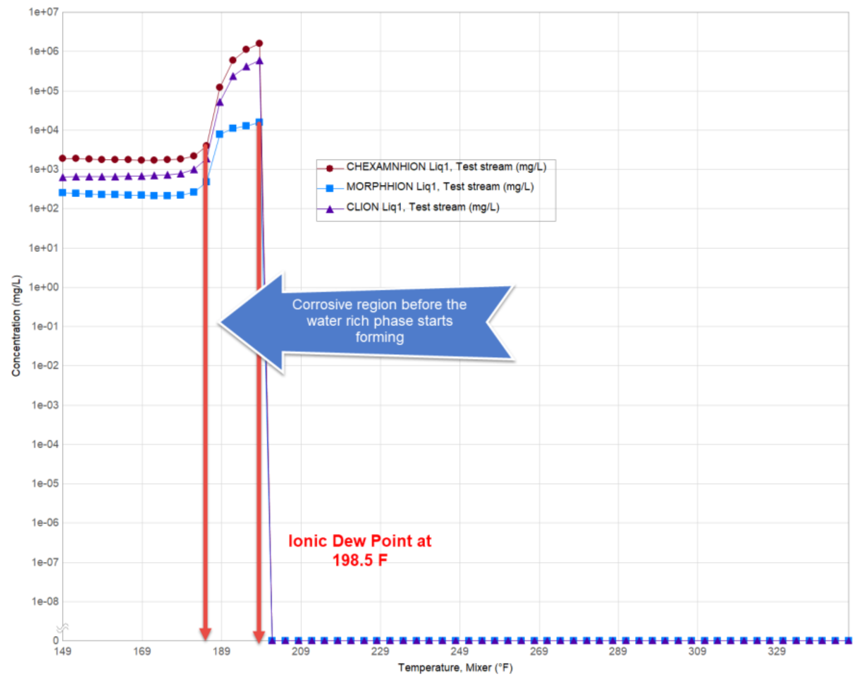


Figure 3. Detecting the ionic dew point of morpholine

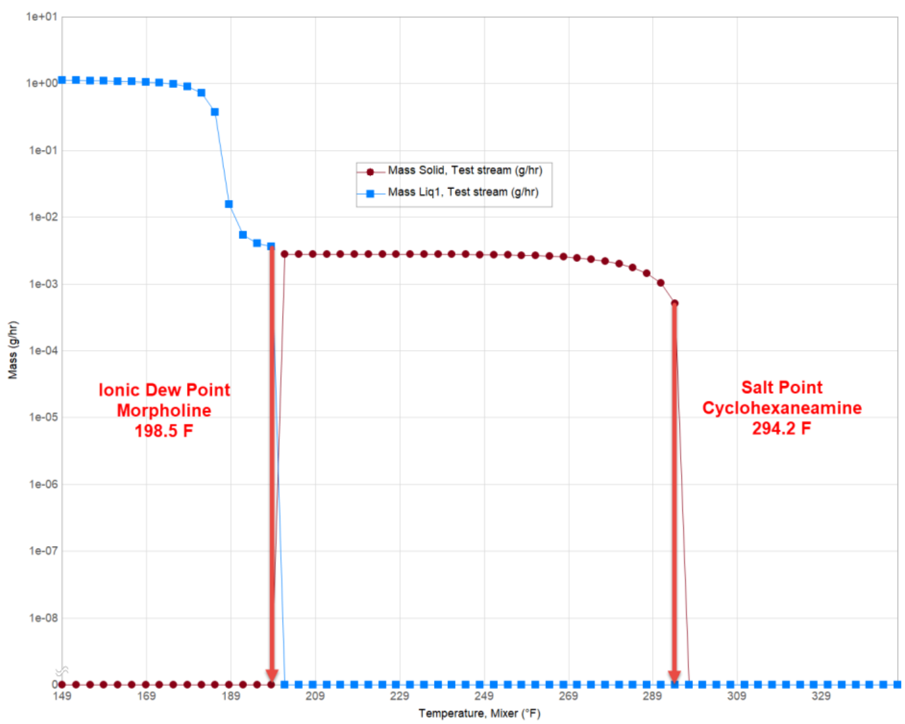


Figure 4. Detecting the salt point of cyclohexaneamine

Simulation analysis

Putting all of the elements of this case together and studying the behavior of the plots, combined onto a single plot in Figure 5.,, we can observe:

294.2 F is the salt point of the cyclohexaneamine
The cyclohexaneamine forms a crystalline solid salt between the temperatures of 294.2 F and 212 F
Morpholine forms an ionic liquid at 198.5 F, effectively marking this as the ionic dew point
Water changes phase at 183.5 F for this set of conditions (due to partial pressures exerted by ionic species)
High amine concentrations cause amine chloride ionic liquid and salt to form

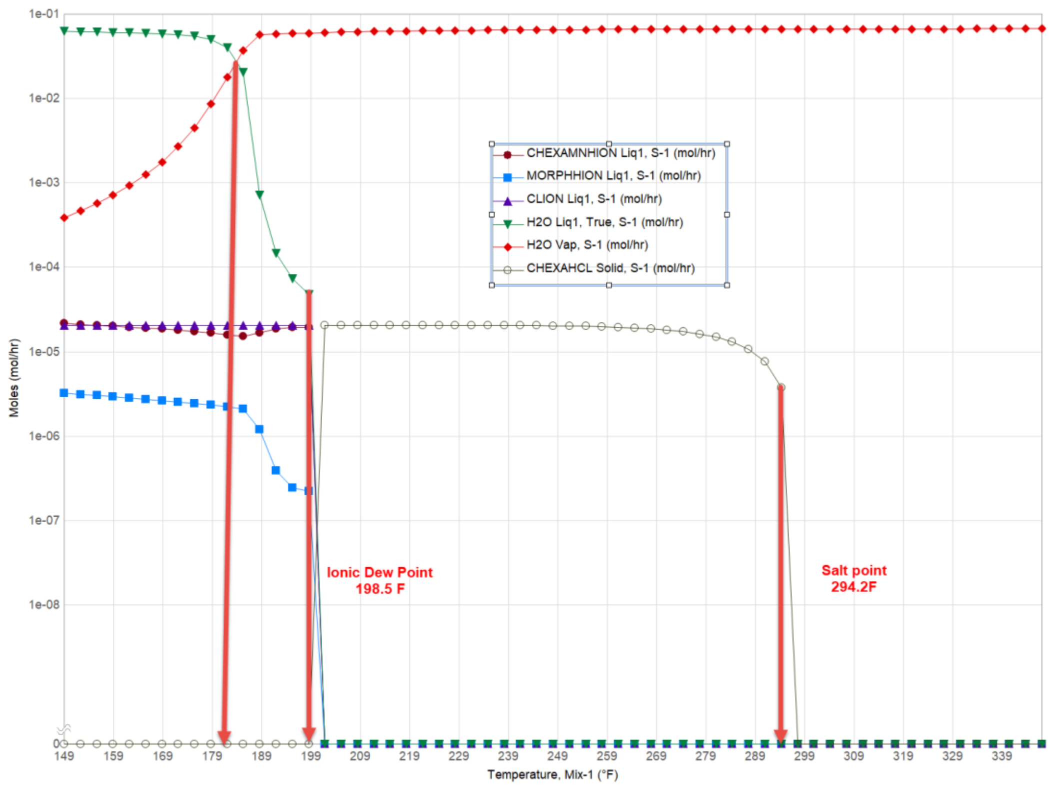


Figure 5. Composite salt point, ionic dew point, and water dew point

Conclusions

Corrosion due to neutralizing amines in refinery overhead systems can cause failures and will affect operating costs. Ionic modeling using the OLI MSE model with amine hydrochloride chemistry enables users to "*Get the chemistry right*." Electrolyte flowsheet simulation successfully predicts the formation of solid salts or concentrated amine hydrochloride solutions, and successful prediction leads to the determination of the three critical operational points needed to optimize this process.

Further work indicated includes modeling the CDU itself, linking the calculations to real-time data, determining the actual corrosion rates of these amine – HCl components (when OLI MSE corrosion becomes available, and studying improvement on the desalter operation – a topic for a future spotlight.

For more Information

- **This case study was presented by Rasika Nimkar, MSc in an OLI Spotlight Seminar, “Refinery overheads salt point” in August 2018.**

  https://www.olisystems.com/webinar

- **OLI Spotlight Seminars are a series of webinars developed by OLI process simulation experts on simulation techniques. Seminars are available on-demand following the live presentation**

Author: Rasika Nimkar, MSc, OLI Client Success Consultant
Contributions by: Pat McKenzie, OLI Vice President Global Sales

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