Mitigating overhead corrosion and reducing downstream costs

A combination of onstream measurements, closed-loop control, and corrosion measurement enabled significant reductions in caustic addition rates and FCC catalyst costs

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Crude tower overhead corrosion can sometimes pose a major challenge for asset operators in maintaining asset reliability and ensuring safe operations for the entirety of a planned run length. The most common cause of initial condensation point (ICP) corrosion is hydrochloric acid (HCl) generated from the hydrolysis of salts present in the crude tower feed. Additional problems, such as under deposit corrosion, result from the HCl reacting with neutralising amines to form salts in undesirable locations. Injecting sodium hydroxide (caustic solution, or NaOH) into the feed stream to the column is one of the measures commonly employed to minimise the generation of hydrochloric acid. Sodium hydroxide reacts with thermally unstable salts present in the crude charge, such as magnesium chloride (MgC_{12}) and calcium chloride (CaC_{12}), to form the more thermally stable sodium chloride (NaCl). Because of its higher stability, NaCl does not hydrolyse readily and reduces hydrochloric acid present in the overhead. Caustic injection for HCl suppression becomes critical in the event of increased salt content in the crude charge or an upset in desalter operation.

Because of its extreme thermal stability towards hydrolysis, most NaCl is normally carried downstream through fractionator bottoms or heavy gasoil streams. Increased sodium content can negatively impact downstream operating units, such as the FCC and coker units. Sources of sodium in these units can originate from residual NaCl in the desalted crude, contribution by caustic injection as described above, and from purchased feeds sent to the FCC unit or coker.

Sodium negatively impacts the FCC unit because it acts as a poison and deactivates the catalyst. The catalyst deactivation rate experienced by the FCC unit increases with sodium concentration in the feed, so sodium entering the unit should always be minimised. In addition to catalyst deactivation, the added sodium lowers the produced gasoline's octane rating, requiring the refinery to pay a penalty for any off-spec product, resulting in lost profit opportunities. The catalyst cost and lost profit can amount to several hundred thousand dollars per year in an average sized refinery. In addition to negative impacts on the FCC unit, there are other downstream concerns surrounding caustic addition occurring in both the crude distillation unit (CDU) and coker. Major concerns include preheat fouling, furnace tube coking, furnace tube cracking, tower foaming, sodium contamination, and accelerated corrosion. As a result, any condition that increases or reduces sodium levels running to these units would benefit from proactive control or systematic optimisation of the caustic injection rate to ensure that sodium concentration is minimised.

It is important to note that the savings in catalyst costs and gasoline octane number discussed above can only be effectively achieved if mitigation of CDU overhead corrosion is effectively preserved. In other words, if mitigation is not effectively maintained during proactive variations to caustic injection rate, the cost of increased overhead corrosion could exceed any potential downstream savings.

Overview

This article presents a case study demonstrating how the risk of crude tower overhead corrosion was monitored and managed using a state-of-the-art crude corrosion management tool called SafeZone, which allowed the overall caustic injection rate to be minimised. By maintaining effective overhead corrosion mitigation while simultaneously minimising caustic usage, significant savings were achieved downstream and are quantified here. The following study outlines all key performance indices that SafeZone tracks affecting corrosion risk and demonstrates how tower overhead corrosion risk was minimised while caustic injection rate was simultaneously reduced.

SafeZone is an automatic and virtually autonomous platform for salt point analytics that not only enables reliable and rapid computations of all amine hydrochloride salts that could potentially form in the system but also facilitates a constraint optimisation scheme surrounding the ongoing and dynamical identification of maximum amine and chloride concentration thresholds needed to prevent salt formation in the system. Furthermore, the tool recognises variations in both operational and chemistry data and translates those variations into salt point temperature variations. These computations allow reliable prediction of safe operational ranges. SafeZone also computes sensitivities of salt deposition temperatures to changes

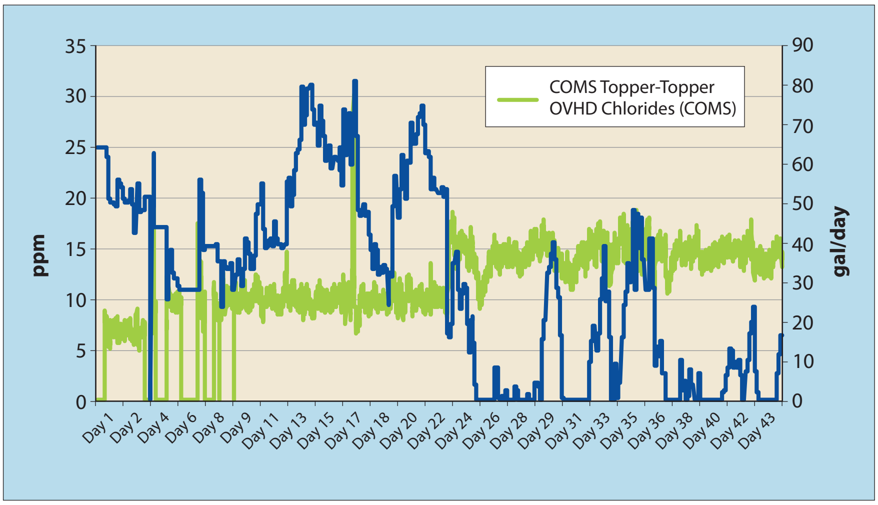

Figure 1 Reduction in caustic injection rate resulting in an elevated level of chlorides in crude tower accumulator boot water

Comparison of the computed amount of metals in the FCC unit feed between the base case and reduced caustic case

Calculation results	Base case	Reduced caustic	% Reduction
Sodium to crude unit fractionator, lb/day	28.48	16.74	41%
Sodium in crude tower bottoms, wtppm	2.33	1.37	41%
Sodium in FCC unit feed, lb/day	29.75	18.04	39%
Sodium in FCC unit feed, wtppm	1.42	0.86	39%

Table 1

in operational and chemistry variables, allowing the user to perform a 'what-if' analysis concerning any of the variables impacting salt-induced corrosion. More importantly, SafeZone performs many calculations of salt deposition temperature for variations around average values for operational variables and translates this into a reliable indicator called the salting probability index (SPI). The SPI accurately reflects changes in the severity of salt precipitation from one day to the next and is driven by operational and feed composition changes.

The purpose of this study is to provide an estimation of the value of savings in FCC catalyst made during the optimisation of overhead corrosion and associated caustic rate reductions. The estimated savings in the catalyst cost provide a benchmark against which the cost of running the SafeZone program can be compared.

Opportunity

A Gulf Coast refinery utilised both SUEZ's overhead onstream sensor and controller package, COMS (Crude Overhead Management System), and SafeZone to minimise corrosion risk to the crude overhead. By using closed-loop automated control of caustic injection via the COMS system, chloride fluctuations are dramatically reduced, and chloride levels can then be specified as a control variable (see **Figure 1**). Because there was no vacuum tower in operation, the atmospheric tower bottoms from the crude unit combined with purchased gasoils make up the FCC unit feed. The purchased feed was often contaminated with ballast water while in transit, causing increased levels of salts. As a result, the sodium concentration in the FCC unit feed was relatively high and trending upwards. Using both COMS and SafeZone, it was possible to continually monitor key performance values automatically and make ongoing selective manipulations to minimise corrosion risk while simultaneously minimising caustic usage. This was made possible because opportunities were often identified that allowed the ongoing dynamical adjustment of chloride levels to the minimum amount needed to negate the risk of ongoing salt precipitation. By lowering caustic injection rates during any such safe opportunity, deactivation of the FCC catalyst from sodium poisoning and the impact of increased sodium on gasoline octane number and other downstream impacts were minimised.

Figure 1 illustrates one such opportunity for caustic reduction by upwards optimisation of the chloride setpoint. In this case, SafeZone identified the upper safe limit during this period as 15 ppm HCl in the boot water, while the actual concentration averaged about 10 ppm. By reducing the caustic injection rate by 80%, from an average of 50 gal/d to about 10 gal/d, the system was controlled to the upper safe limit while reducing sodium content in the FCC unit feed.

FCC unit cost saving from the reduction in caustic injection rate

The following describes the estimation of savings in FCC catalyst costs. The basic premise of the estimation method is the evaluation of incremental costs due to increased catalyst use arising from catalyst deactivation caused by sodium poisoning. Before and after the reduction in caustic rate, catalyst rates were estimated daily to calculate the incremental cost in annual catalyst use.

The first step towards estimation is computation of the amount of sodium in the FCC unit feed for the base case and reduced caustic case. Since a vacuum tower was not operational in the refinery, there was no contribution to the total sodium content from the vacuum tower bottom stream or from a heavy vacuum gasoil (HVGO) stream. Therefore, contributions towards the total sodium content were based only on sodium in the atmospheric tower bottom stream and purchased feed. The results are shown in **Table 1**.

From the results presented in **Table 1**, it can be seen that reducing the caustic injection rate resulted in a reduction of sodium in the CDU feed from 28.5 lb/d to 16.74 lb/d. With the salt content in the purchased feed remaining constant, the sodium content in the FCC feed reduced from 29.8 lb/d to 18 lb/d, which is equivalent to a reduction from 1.42 wtppm to 0.9 wtppm. In **Table 2** the contributions to total sodium content in the FCC feed are also compared for the base case and reduced caustic case. It can be seen that, after caustic rate reduction, the contribution from caustic injection dropped from 48.4% to 14.8%, while the contribution from crude increased from 47.3% to 78.0%.

A reduction in caustic injection rate resulted in an estimated reduction in fresh catalyst utilisation from 4.77 t/d to 4.23 t/d, around an 11% reduction in catalyst usage. Although this reduction in fresh catalyst utilisation does not seem significant on a per-day basis, based on catalyst cost of $2500/t of catalyst and 365 days of operation of the FCC unit, the drop in catalyst utilisation amounts to annual catalyst cost savings of $497 149. On the basis of a reduction in pounds of caustic per thousand barrels of crude, this amounted to a reduction of 2.53 t/d of fresh catalyst usage. This is equivalent to annual catalyst cost savings of $2.31 million per thousand barrels of caustic injection rate reduction.

Relative sodium contribution to FCC unit feed by source

Calculation results	Base case	Reduced caustic
Sodium from crude, %	47.3	78.0
Sodium from caustic, %	48.4	14.8
Sodium from purchased feed, %	4.3	7.2

Table 2

Conclusion

1. Utilising a combination of onstream measurements, closed-loop control, and an advanced corrosion measurement system enables a greater level of visibility and control of system performance than was previously possible.

2. Because of the tracking of boot water pH, salt deposition temperature, and mixed exit temperature by SafeZone, crude atmospheric tower overhead corrosion was minimised after reducing the caustic injection rate by monitoring key operational variables such as neutraliser injection rate, wash water rate, naphtha pumparound rate, and desalter acid injection rate.

3. Reducing the caustic injection rate by 80% resulted in annual savings of $497 149 in FCC catalyst costs – equivalent to an annual $2.31 million per thousand barrels of caustic injection rate reduction.

Keyur Patel is an Application Expert with SUEZ – Water Technologies & Solutions (USA). With over 12 years' experience in oil and gas, he currently focuses on refinery corrosion including application of chemical products to help refineries maintain reliability and integrity of their assets. He implements monitoring and modelling solutions to detect high corrosion rate events and provides recommendations for mitigation based on industry best practice and product application expertise. He holds a doctorate in chemical engineering.

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