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Navigating corrosion challenges in column overhead systems

Case-by-case methodology as part of best engineering practices, and integration of computer tools as accurate means to predict, identify, and mitigate corrosion issues

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The oil and gas industry invests billions of dollars annually to uphold its integrity. In Europe alone, corrosion imposes a financial toll that costs the economy more than €463 billion per year. In 2013, the European Union reported that corrosion caused more than 20 major refinery accidents since 2000.[1]

Controlling corrosion in oil refining equipment and pipeline systems is very complex, as it involves managing multiple factors in a dynamic system. Typically, corrosion can be minimised when the operating conditions such as composition and phase state, temperature, pressure, equipment selection, metallurgy, and anticorrosion measures are maintained with minimal variation.

However, the industry is facing multiple challenges due to the constant changes in how crude oil and raw materials are processed. The drastic changes in composition, processing philosophy, and flow rates result in varying distribution and degrees of corrosion in the same process equipment and piping. Furthermore, the recent rise in renewable fuel production further complicates refining operations.

Corrosion risks

Currently, there is a growing global trend to produce low-carbon fuels. As biogenic materials are co-processed with crude oil fractions, studying corrosion in refineries attracts attention. Vegetable oil, composed of fatty acids, contains oxygen, which is part of the carboxyl group of the fatty acid molecule, and chlorides. Typically, co-processing happens in hydrotreating units. When oxygen is present, fatty acids produce water (H_2O), carbon monoxide (CO), and carbon dioxide (CO_2).

Furthermore, including chloride-containing groups will form hydrogen chloride (HCl). The reactor effluent will contain these four components. These components may not have been considered in the hydrotreater's original design and material selection. In a diesel hydrotreater using co-processing vegetable oil or animal fats, the reactor effluent needs to be carefully handled to avoid corrosion.

In refinery hydrotreating processes, the reactor effluent system is prone to fouling and corrosion from two main culprits: ammonium bisulphide (NH_4HS) and ammonium chloride (NH_4Cl). To minimise corrosion-related issues, API RP 932-B[2] is a trusted recommendation.

This recommended practice also provides guidelines for the design and operation of reactor effluent air cooling (REAC) systems and addresses velocity limits, metallurgy selection, sour water composition, wash water quality, and rates. However, the industry needs a computer tool that

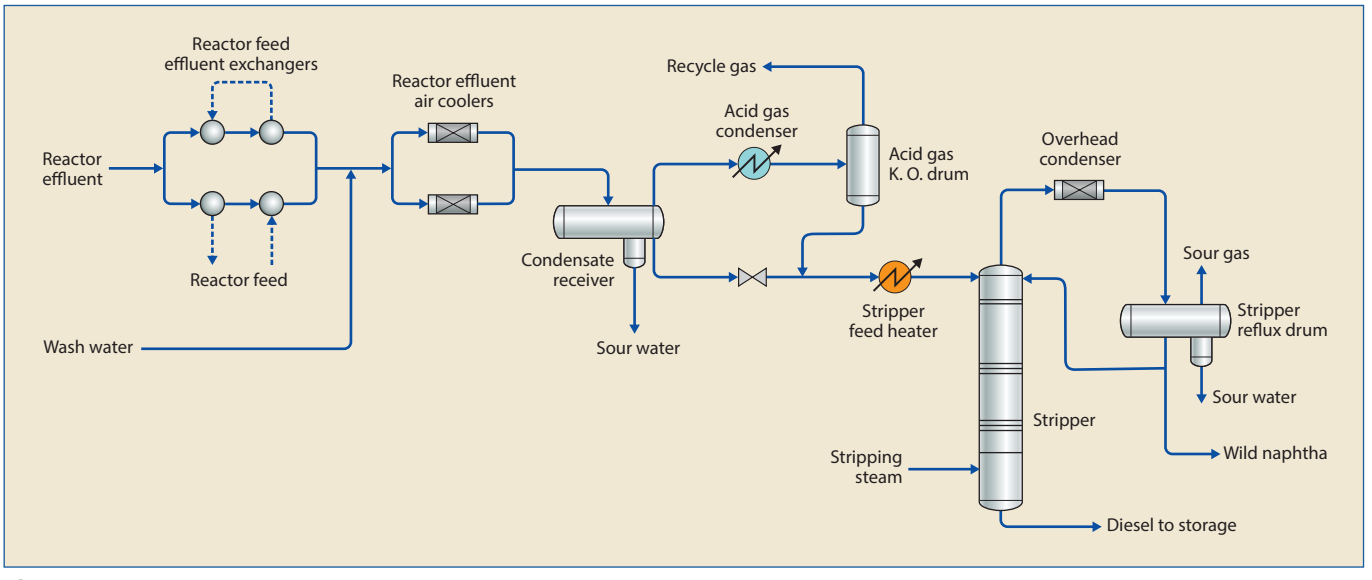


Figure 1 Reactor effluent cooling train and separation plant

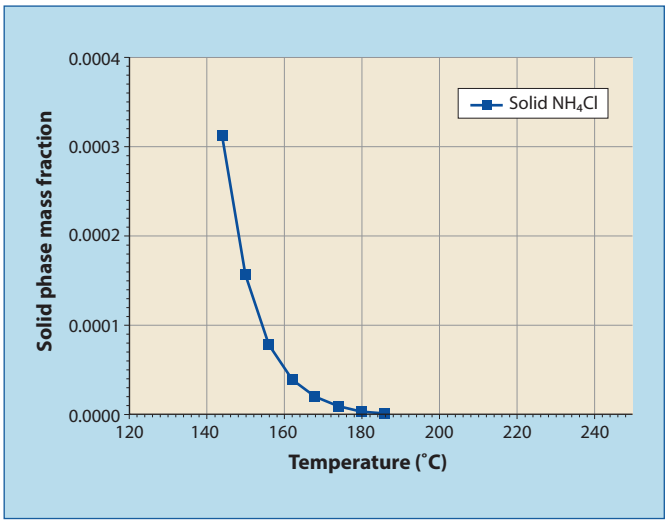


Figure 2 Solid NH_4Cl formation with respect to temperature

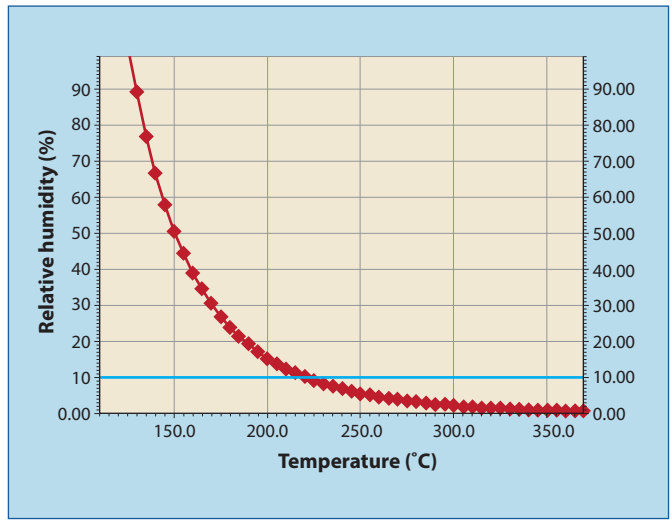


Figure 3 Relative humidity across the feed/effluent exchangers

estimates the formation of corrosive chemicals. With the presence of CO_2 in the reactor effluent, the composition of carbonates (CO_3^{2-}) and pH needs consideration.

A leading process provider has estimated that corrosion accounts for 37% of major issues in hydroprocessing units.[3] For example, corrosion in the REAC alone contributes up to 24% of major corrosion issues. Their study identified the following key contributing factors responsible for corrosion:

❶ Compositional dependant

- Metallurgy
- Nitrogen and sulphur content in the feed
- H_2S and NH_3 partial pressure
- Chloride presence
- Wash water quality and rate
- Vapourise wash water injection points.

❷ Operational dependant

- Fluid velocity
- Balanced and unbalanced headers, the latter causing more corrosion than the former
- Single vs multiple wash water injection points.

Proactively managing corrosion

In operating plants, OLI Systems has developed simulation technology that rigorously calculates corrosion-causing electrolyte species. To cater to the industry's specific needs, KBC's proprietary Petro-SIM simulation software now integrates into the powerful OLI thermodynamic engine. This strategic integration enables process, materials, corrosion, and plant integrity engineers to:

- Enhance the electrolyte chemistry simulation capabilities
- Predict general corrosion
- Estimate localised corrosion
- Simulate corrosive environments
- Identify and debottleneck corrosion issues
- Manage corrosion.

Simulation results support and validate recommendations to mitigate corrosion, such as:

- Detailed assessment to determine corrosion issues sitewide
- Enhanced use of neutralisers, inhibitors, anti-fouling additives, chloride control, and wash water facilities
- Metallurgical upgrades and adding new equipment when operating solutions are impractical.
- Robust analysis program to monitor and control process conditions.

The wash water's flow rate and quality are critical to prevent increased corrosion and deposition of NH_4HS and NH_4Cl. The following case studies aim to analyse how these two variables affect corrosion prevention in refineries.

Case study: Renewable diesel plant

With the growing tendency to produce fuels with a low carbon footprint, co-processing vegetable oil with crude oil fractions is attracting attention to study corrosion in refineries. Vegetable oil contains oxygen, which is part of the carboxyl group of the fatty acid molecule. Co-processing is typically done in hydrotreating units, and the oxygen in fatty acids will produce H_2O, CO, and CO_2. These three components will now be part of the reactor effluent composition.

Originally, the hydrotreater's design and material specifications may not have considered these components. For example, in a diesel hydrotreater with 15 vol% co-processing of vegetable and animal oils (11 wt% palmitic acid, 23.4 wt% oleic acid, 53.2 wt% linoleic acid, 7.8 wt% linolenic acid, 4 wt% stearic acid, and others), the reactor effluent may have approximately 2.2 mass% of CO, 2.0 mass% of CO_2, and 1.2 mass% of H_2O. The vegetable oil is assumed to be pretreated for this case study, as it is a typical practice to eliminate chlorides and phosphorous. The reactor effluent cooling train and separation plant are shown in **Figure 1**.

When the reactor effluent stream contains approximately 30 ppm-wt% of HCl, it is important to determine whether solid NH_4Cl can form in this stream when it leaves the reactor precooling system at 250°C (482°F). This can be achieved by using the Petro-SIM modelling software and the OLI thermodynamic engine. **Figure 2** shows that solid NH_4Cl is imminent inside the REAC, and corrective action is necessary based on these results.

The corrective action normally involves injecting wash water, generally sour water.[4] As a result of the computer model, the optimum amount of wash water to use is approximately 0.09 kg of reactor effluent when stripped sour water

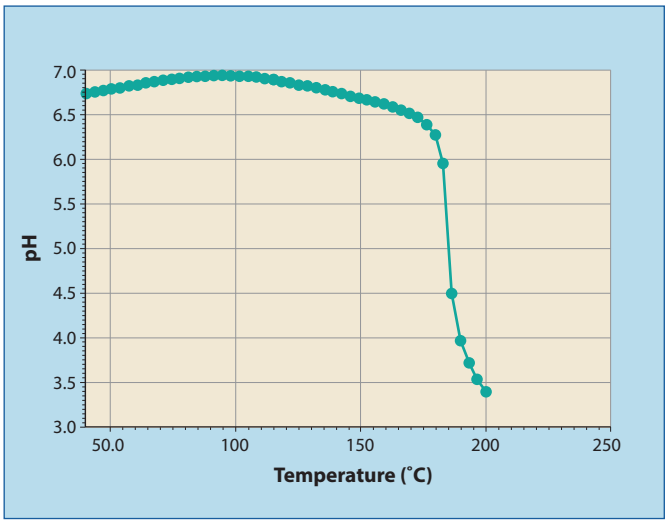


Figure 4 pH dependency with temperature in the REAC

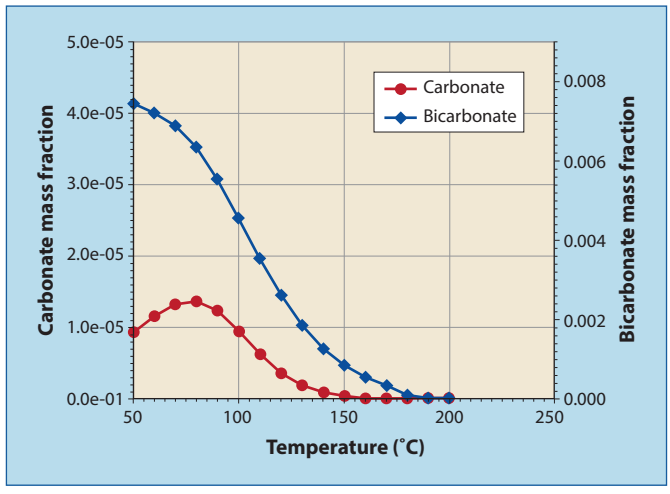


Figure 5 Bicarbonate and carbonate concentration as function of temperature in the REAC

is applied with 5 ppm of H_2S and 40 ppm of NH_3, with 25 wt% of water phases. The specific outlet temperature of the REAC will significantly affect the physical properties of the sour water.

Another important parameter to estimate is the potential for salts to form in the feed/effluent exchangers that absorb water from the hot effluent vapours. If NH_4Cl salts get wet, they form pits, known as pitting corrosion. In addition to causing metal loss that can develop leaks, pitting corrosion creates weak points in the metal structure that may cause cracks. Therefore, operators need to know under what conditions the NH_4Cl salts can get wet to prevent this issue.

The relative humidity (RH) parameter is used by corrosion specialists to calculate if NH_4Cl salts will absorb water from the hot vapour stream. RH is calculated by obtaining the ratio of the partial pressure of water in the vapour stream and the saturated pressure of water at the process temperature, then multiplying it by 100%. NH_4Cl salts will start to absorb water from the vapour stream when the RH reaches at least 10%, with values between 30% and 50% showing the highest degree of absorption.

In this case study, RH has been plotted across the temperature difference on the process side for the feed effluent exchangers. The 10% RH threshold is surpassed once temperatures get below 225°C. From the graphs in **Figures 2** and **3**, we can infer that the potential for salts to form and start to get wet happens at the NH_4Cl formation temperature.

Therefore, the risk of corrosion and fouling significantly increases at temperatures below 190°C. We conclude that when the outlet temperature of the feed/effluent exchangers stays at the current temperature of 250°C, then the NH_4Cl salts will only form at the REAC, and the potential for the salts to get wet is mitigated with a proper water wash that will completely dissolve the salts.

According to the Alkaline Carbonate Stress Corrosion Cracking (ACSCC) guidelines,[5,6] the four conditions promoting corrosion in sour water systems are: a) presence of an aqueous phase, b) pH above 8, c) carbonates content (CO_3^{2-}) above 100 ppm-wt, and d) piping not post-welding heat treated.

Figure 4 shows the dependence of the pH with respect to temperature. In this case, the pH falls below 8. Additionally, the computer model can estimate the formation of bicarbonate (HCO_3) and CO_3^{2-}, shown in **Figure 5**, and the concentration of CO_3^{2-} does not exceed the ACSCC guidelines.

The analysis is extended to the overhead system of the stripper, which includes the overhead condenser and the stripper reflux drum. The evolution of the pH in the

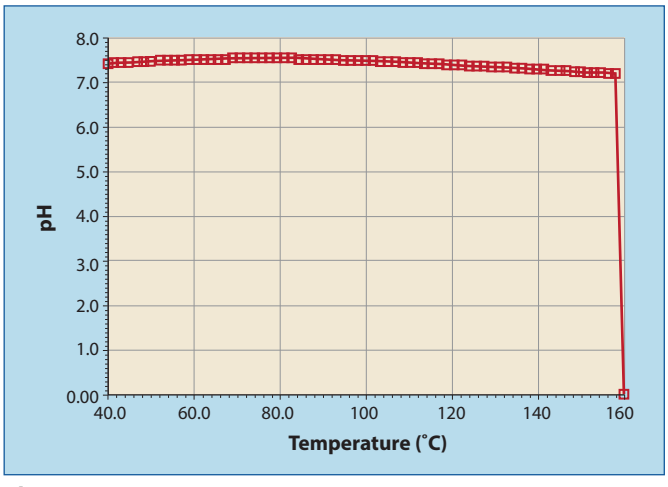


Figure 6 pH dependency with temperature in the overhead condenser

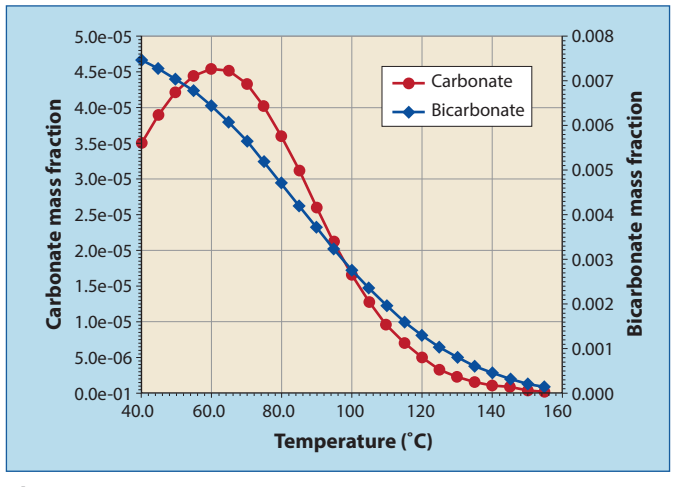


Figure 7 Bicarbonate and carbonate concentrations as function of temperature in the overhead condenser

overhead stream in the overhead condenser is presented in **Figure 6.** Simulation results show that the maximum pH is still below 8. **Figure 7** shows that the bicarbonate and carbonate compositions are a function of temperature in the overhead condenser. The computer model predicts a carbonate composition below 50 ppm-wt. Again, the aqueous phase formed in the splitter overhead system does not pose any risk for alkaline carbonate stress corrosion, based on the ACSCC guidelines.

Conclusion

The oil and gas industry faces significant challenges in controlling corrosion in refining equipment and pipeline systems, with the complexity escalating due to the evolving processing of crude oil and the rise of renewable fuel production. Particularly in Europe, the financial toll of corrosion emphasises the need for effective corrosion management strategies.

As shown in this case study, vegetable oil and animal fats containing carboxyl groups could cause carbonate stress corrosion, emphasising the need for careful engineering analysis. The case study demonstrated the limits established by the ACSCC guidelines.

This article recommends using a case-by-case methodology as part of best engineering practices. Integrating computer tools, such as Petro-SIM software with OLI systems, provides a robust and accurate means to predict, identify, and mitigate corrosion issues in refineries.

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