HP | Catalysts

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Understanding HCN in FCC: Formation, effects and mitigating options

In these challenging times, fluidized catalytic cracking units (FCCUs) aim to improve margins by processing poorer- or different-quality feeds, while maintaining good yield performance. These feeds may produce more coke and have elevated nitrogen levels, which can then increase the potential for higher cyanides and associated equipment damage in wet hydrogen sulfide (H_2S) service.

A general overview of cyanide formation and associated corrosion problems in the catalytic fractionator and gas plant is provided to help explain the nature of the problem and what mitigating actions can be taken. Many FCCUs have no history of cyanide-related problems, as potential cyanide effects are adequately controlled by water washing and by using chemical additives.

In addition, unit operating parameters can be adjusted to help control cyanide production. Application of this approach is discussed for a unit that observed higher cyanides in the catalytic fractionator overhead water following increased processing of heavier feeds enabled by a catalyst change. An in-depth investigation showed that the amount of cyanides was increasing with the heaviness of the feed. This unit subsequently found no cyanide-related problems during a unit turnaround inspection.

Wet H_2S equipment damage mechanism. In wet H_2S service, atomic H° is formed in the steel corrosion reaction, as indicated in **FIG. 1.** The presence of H_2S in water inhibits the recombination of the atomic H°, and potentially enables these atoms to penetrate into and diffuse through the equipment steel.

The atomic H° can combine inside the steel to form molecular H_2, which causes these larger structures to be trapped and unable to diffuse back out. The H_2 can then cause damage to the steel in the form of blistering, sulfide cracking, H_2-induced cracking and stress-oriented H_2-induced cracking. However, under normal circumstances, the iron sulfide (FeS) scale formed on the steel surface in a wet H_2S environment provides a barrier to the atomic H° produced, thereby generally mitigating the issue.

HCN and potential for wet H_2S damage. Hydrogen cyanide (HCN) and ammonia (NH_3) from the FCC reactor leave in the catalytic fractionator overhead product, and free cyanide ions (CN^-) are formed in water by the reaction HCN (aq) + NH_3 (aq) $\leftrightarrow NH_4^+$ (aq) + CN^- (aq). The CN^- tends to remove the FeS scale on steel surfaces by forming a ferrocyanide complex, which is soluble in water by the reaction FeS + $6CN^- \rightarrow Fe(CN)_6^{4-} + S^{2-}$. Removal of the scale then allows atomic H° to diffuse into the steel, leading to wet H_2S damage, as previously described.

Experience shows that hydrocyanic acid in the overhead water does not cause significant metal loss, as NH_3 absorbed with the HCN acts as a buffer, typically keeping the water pH above 8.

Locations prone to cyanide corrosion. A typical catalytic fractionator overhead system with water wash injection used as a corrosion mitigation measure is shown in **FIG. 2.** Locations most prone to cyanide corrosion problems are circled.

Industry experience shows that if wet H_2S damage occurs, it is most frequently observed in the vicinity of the compressor coolers and absorber tower due to high HCN in the gas streams vs. hydrocarbon liquids and in the deethanizer tower. Reported problems have been related to changes in feed quality (e.g., high nitrogen, low sulfur), which required adjustment to corrosion control measures, inadequate water wash rates, poor distribution of water upstream of coolers, and poor separation of hydrocarbons and water.

HCN limits and measurement of free cyanides. A typical guideline is to maintain free cyanides (HCN and CN^-) in sour water below 20 ppm (mg/l) for corrosion control. However, it is relatively difficult to accurately measure free cyanides due to a number of potential interferences. Measuring total cyanides includes both free cyanide plus stable cyanide compounds, which do not form a weak acid and do not "complex" FeS scale. Total cyanides measurement would be expected to over-estimate free cyanides and the related concern for wet H_2S damage.

Some FCCUs have reported elevated total cyanides close to 100 ppm, and no cyanide-related problems have been experienced. Polysulfide has been successfully used for many years to control high cyanide levels.

HCN formation chemistry. Various organic nitrogen (N) compounds are present in FCC feed. Some HCN may form in the FCC riser due to reactions such as $NH_3 + CO \rightarrow HCN + H_2O$, for
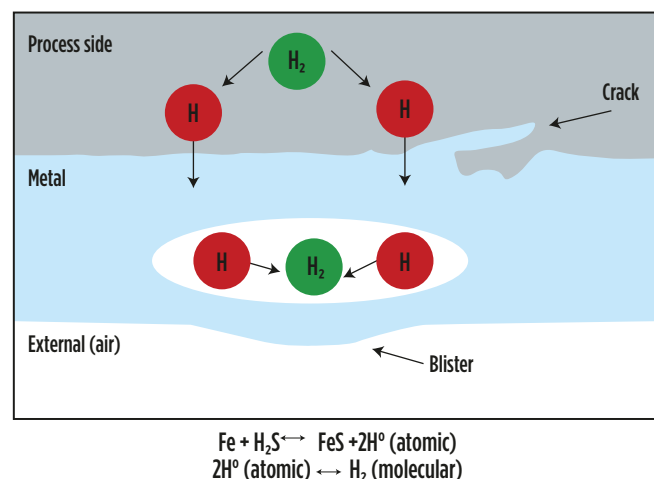

$$Fe + H_2S \longleftrightarrow FeS + 2H° \text{ (atomic)}$$
$$2H° \text{ (atomic)} \longleftrightarrow H_2 \text{ (molecular)}$$

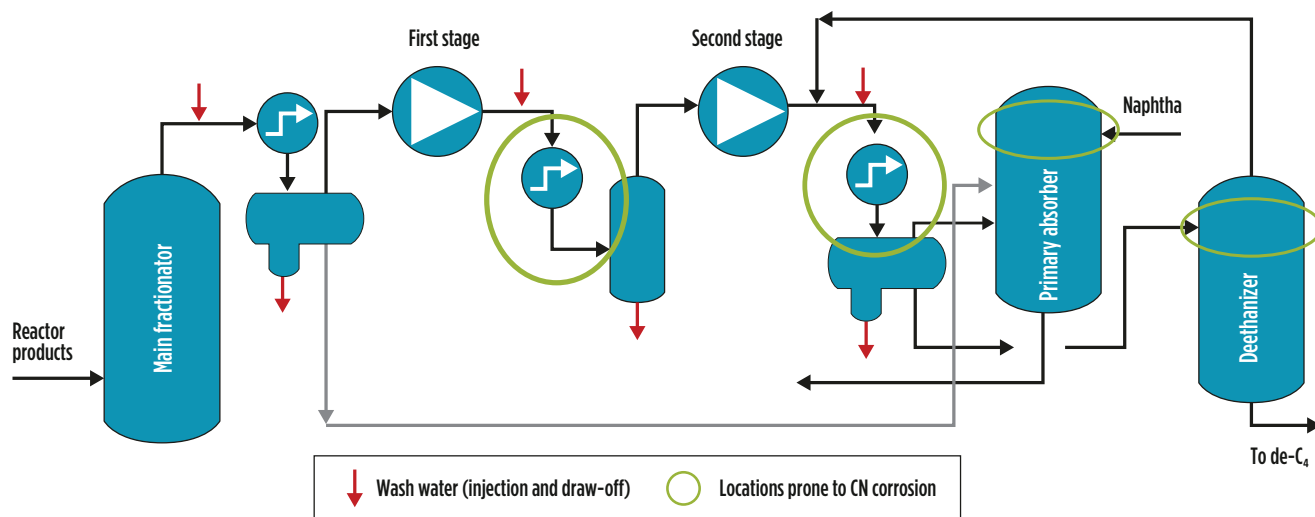**FIG. 1.** Steel corrosion reaction and damage caused by H_2.

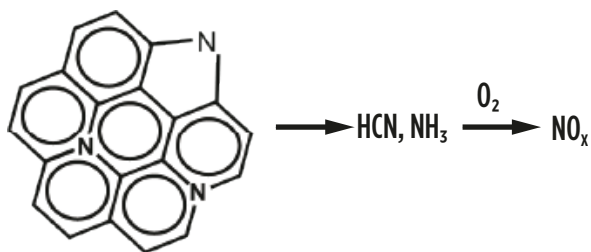**FIG. 2.** Locations prone to cyanide corrosion damage.

FIG. 3. HCN formation.

example. However, a significant amount of the HCN is also being entrained with the catalyst circulated back to the riser from the regenerator. Coked catalyst from the reactor, containing C, H, S and N, is sent to the regenerator, where the coke is burned off. Here, HCN and NH_3 are formed as intermediate products from coke N reactions and are oxidized to N_2 and NO_x products given adequate time, temperature and O_2 availability (**FIG. 3**).

FCC coke consists of coke from four main sources:

1. Catalytic reactions
2. Metal dehydrogenation reactions
3. Hydrocarbons adsorbed/entrained in the catalyst pores from the stripper (strippable)
4. Feed additive (Conradson carbon residue is a measure).

"Hard" coke formed by catalytic reactions would tend to be highly stable aromatic hydrocarbons formed deep within catalyst pores. This type of coke would be more difficult to burn off in the regenerator vs. other sources of coke. It suggests that the amount of HCN formed will depend on the source of the FCC coke, as well as the type of N compound in the feed and operating conditions.

HCN in fractionator overheads. Feed quality and reactor operating conditions influence the amount of N in coke and coke burned and, therefore, the potential for increased HCN. The amount of HCN entrained from the regenerator to the riser depends on the catalyst circulation rate, the gas volume entrained, and the regenerator operating conditions leading to HCN formation.

All of these factors will be discussed in more detail by reference to a case study for Refiner A that experienced increased HCN

in the catalytic fractionator overhead system following a catalyst technology switch. Improved delta coke enabled a significant increase in heavier feed (as measured by feed concarbon) and catalyst/oil ratio, which resulted in higher HCN, as shown in **FIG. 4.** "CN control" shows data after actions were taken by the refinery to maintain total cyanides below a limit set for the unit.

Feed quality and HCN formation. Typically, 50%–75% of feed concarbon goes to coke and increases the potential for HCN production due to an increase in coke burning.

FCC feed total N typically ranges from 500 ppm–2,000 ppm (basic N comprises approximately one-third of the total). As shown in **FIG. 5,** feed total N correlated with feed concarbon for this unit.

Feed N is distributed throughout the FCC reactor products, with approximately 40%–50% of the N ending up in coke. The distribution depends on the types of N compounds present in the feed and on the operating conditions. For example, concarbon coke may contain more N compounds that can form HCN under regenerator conditions than catalytic coke.

Regenerator operating conditions. Refiner A operates a partial CO burn regenerator. Partial CO burn regenerators typically operate with 4%–7% CO in the flue gas, and lower O_2 concentration in part of the bed would be expected to reduce conversion of HCN to NO_x. HCN levels tend to be very low when the regenerator is operating in full CO burn; i.e., there is an excess of flue gas O_2, and HCN can be fully oxidized in this mode.

FIG. 6 shows total cyanides in overhead drum water vs. some regenerator operating variables for Refiner A's FCCU. Three data sets are shown:

1. "Other supplier" period represents the baseline when a non BASF catalyst was in use
2. "All" period documents the effects of the change to a low-delta-coke catalyst[a], which allowed Refiner A to expand the envelope of its operations to feed concarbon above the historical maximum of 4 wt%, while increasing the catalyst circulation rate
3. "CN control" period shows how Refiner A was able to

mitigate the CN level while maintaining the advantages offered by the low-delta-coke catalyst[a].

Process variables interact on an FCCU, making it sometimes difficult to isolate the effects of one variable. For example, higher feed concarbon tends to increase regenerator bed temperature at constant feed preheat and lead to a reduction in catalytic circulation rate, as shown in **FIG. 6.** Although higher regenerator bed temperature and lower catalytic circulation rate might be expected to reduce HCN, the percentage of CO in flue gas was the dominating variable for controlling HCN production. **Note:** Wash water rates were maintained within the normal operating range.

This unit has some regenerator design shortcomings due to expanding capacity over the years, emphasized by the high feed concarbon intake with insufficient residence time to complete HCN conversion, inefficient catalyst/air distribution leading to localized regions of O_2 deficiency/low bed temperatures, potential short-circuiting of catalyst high in HCN directly to the outlet, etc. At the same time, these issues highlighted the potential to further optimize the unit design to enable the full concarbon intake offered by the catalyst[a].

Measures to reduce HCN production.

Other operational changes that may be considered for reducing HCN are to increase O_2 partial pressure and gas/catalyst residence time by raising regenerator pressure and catalyst bed level. Use of additives to promote the conversion of C to CO_2 is also known to increase NO_x emissions.

Some experimental work indicates that use of a CO promoter will reduce HCN as it is converted to N_2 or NO_x. The CO promoter would be expected to be more effective for reducing HCN in a full CO burn environment.

Changes to the regenerator design can also be considered to reduce HCN by increasing conversion. Some examples are providing more air near the spent catalyst inlet to increase O_2 availability and regenerator bed temperature in this zone where HCN is initially formed, and improving the distribution of catalyst to achieve optimal contacting and minimize localized zones of high CO.

Corrosion control and monitoring for wet H_2S damage.

As previously indicated, wash water is commonly injected into the overhead gas streams to reduce cyanide and ammonium levels. In addition, many North American FCCUs processing high-N feeds supplement water washing with ammonium polysulfide (APS) injection, which has enabled satisfactory operation with very high cyanide levels above 100 ppm in water. Some FCCUs also use filming inhibitors for corrosion control.

Various water wash schemes are used. Condensate is commonly injected upstream of the first-and second-stage compressor coolers. Some FCCUs also inject wash water upstream of the catalytic fractionator overhead condensers to supplement condensed reactor steam and water that may be recycled from the overhead drum back to the condensers. To achieve optimal water/gas contacting for maximum HCN removal, it is important to provide suitable water spray nozzles and efficient water distribution systems across multiple exchanger banks (if present).

Cyanides are more soluble in water at higher pressures; therefore, injecting water upstream of the compressor coolers is the best location to maximize HCN removal from gas. It also promotes mixing of the water and gas in the cooler itself. FCC wash
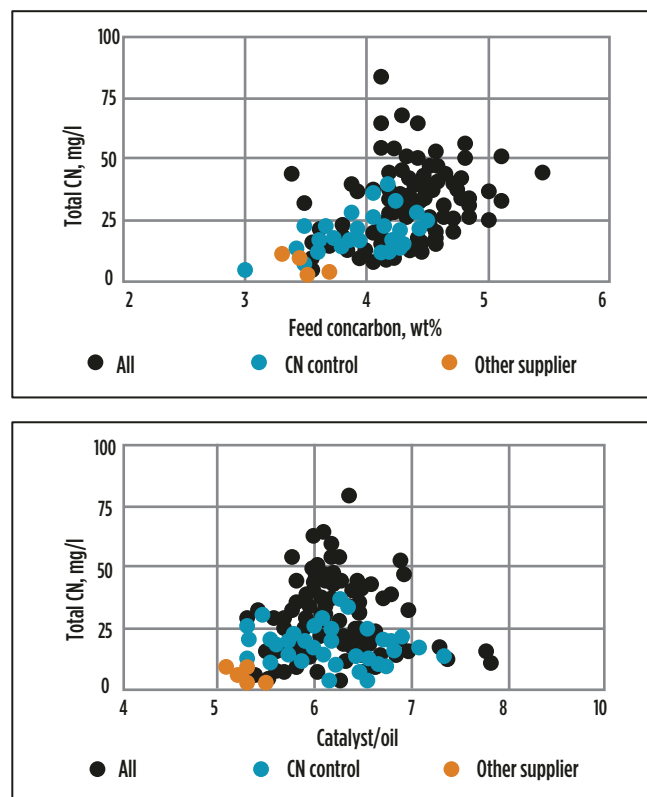

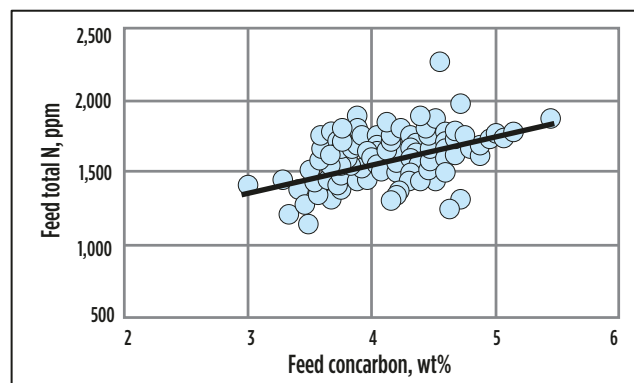**FIG. 4.** Processing heavier feed with increased cyanides.

FIG. 5. Feed total N vs. feed.

water rates are typically in the range of 1 gal/min–2 gal/min of water/1,000 bpd feed (0.034 m^3/m^3 feed–0.068 m^3/m^3 feed) to maintain an acceptable concentration of free cyanides in water. The preferred scheme is to send water collected from the higher-pressure drums directly to the sour water stripper, as sending water back to the catalytic fractionator drum can set up an HCN recycle in the gas due to flashing off at the lower drum pressure.

APS appears to react with the FeS scale to help form iron bisulfide (FeS_2), which is more resistant to complexing with HCN. APS is typically added to the wash water to maintain a low excess ppm level and to ensure that the water samples have an amber color. If the FeS scale no longer provides protection due to high cyanides and insufficient APS dosage, then Prussian blue deposits (indicative of ferrocyanides) are observed in the water samples.

Filming inhibitors minimize the impact of corrosion by providing a thin barrier on surface equipment and reducing the formation of H° atoms through the use of specially designed filming inhibitor chemistries. The filming inhibitor must effectively cover all equipment surfaces by using efficient dispersion systems as for water washing and APS.

Many FCCUs have no history of cyanide-related problems. However, closer monitoring may be warranted if significant changes in feed quality (e.g., higher concarbon/N and/or operating conditions) are observed. Several options for monitoring the likelihood of wet H_2S damage occurring can be considered. Water can be analyzed for total and free cyanides in water and the water color can be checked, as a Prussian blue color would indicate that the HCN has removed some FeS scale. Routine onstream ultrasonic thickness measurement (UTM) from the outside of susceptible equipment can be performed, and H_2 patch probes can be used to detect an increase in H_2 flux through metal walls.

Takeaway. A change to a low delta coke catalyst[a] at Refiner A demonstrated that FCC profitability can be improved by increasing heavier feed processing while expanding the envelope of the operating parameters, even if poorer feed quality gives rise to increased cyanide production and potential risk of wet H_2S damage. A combination of monitoring, cyanide corrosion control and adjustment of operating parameters is available to mitigate the risk, instead of giving up on improved economics, while unveiling the potential for further FCC regenerator design optimizations. **HP**

NOTE

[a] BASF catalyst

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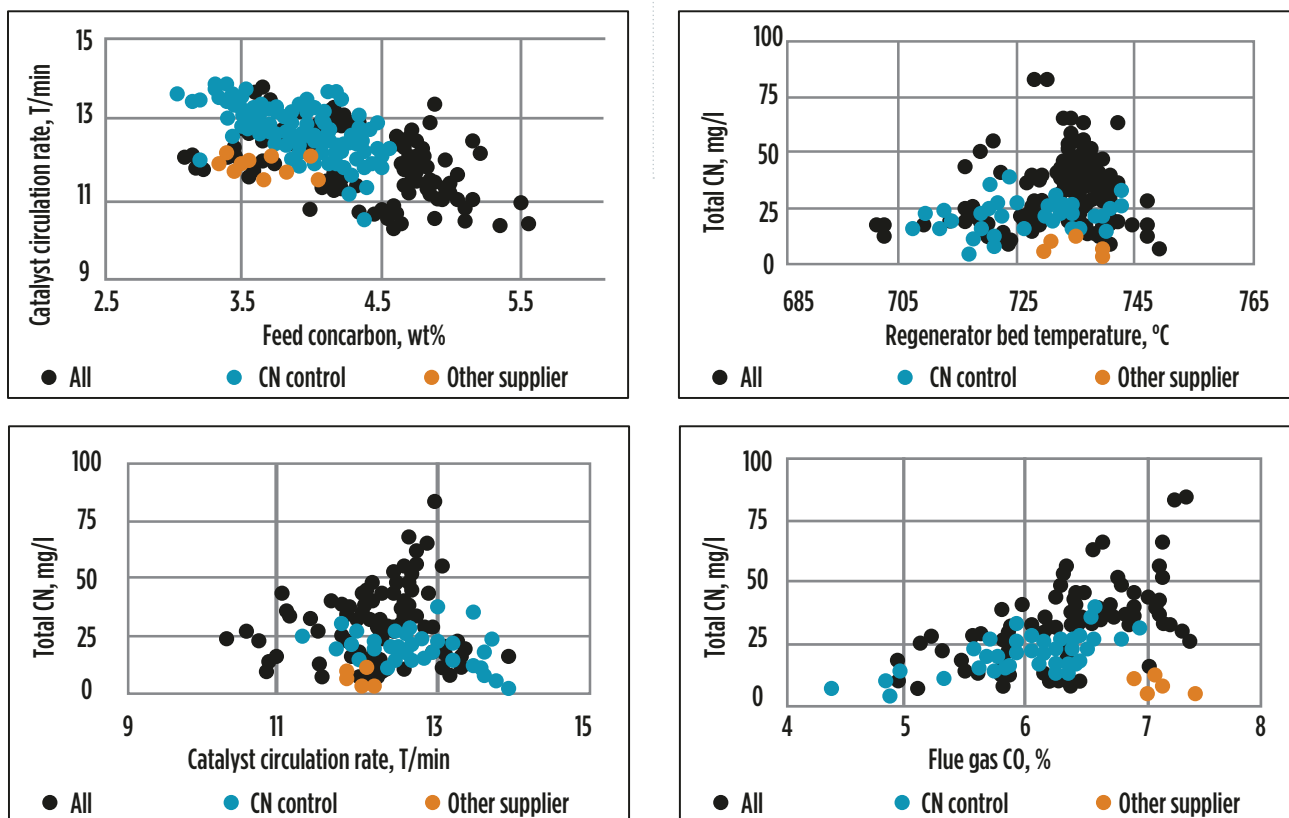
FIG. 6. Regenerator operating parameters.